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WARREN DE LA RUE, PH.D., F.R.S.
THOMAS GRAHAM, F.R.S.

W. A. MILLER, M.D., F.R.S.
J. STENHOUSE, LL.D., F.R.S.

Editor :

HENRY WATTS, B.A., F.R.S., F.C.S.

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JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—On *Pyrophosphotriamic Acid*.

By J. H. GLADSTONE, Ph.D., F.R.S.

It was my intention, in conjunction with my assistant and friend, Mr. J. D. Holmes, to follow up our previous papers on some of the amides of phosphoric acid* with a more complete investigation of the whole subject. But our paper on the action of ammonia on sulphochloride of phosphorus was scarcely printed, when Mr. Holmes was taken seriously ill, and his death, last midsummer, has deprived the world of a careful experimenter and a good man. I feel his loss the more because he had many thoughts and observations connected with these compounds of phosphorus, which he never committed to writing. On looking over our notebooks, I find a tolerably complete history of a remarkable acid amide, which, with a few additional experiments, will form the present communication.

If dry ammonia gas be allowed to stream slowly into a flask containing oxychloride of phosphorus, kept cool by being immersed in water, the liquid is gradually converted into a white solid mass by the absorption of two equivalents of ammonia. If at that point the flask be immersed in water at 100° C., the mass will be found capable of absorbing two more equivalents of ammonia, and on the addition of water to the white substance thus produced, there results an insoluble amide, the subject of the present inquiry. In order to obtain it pure, the oxychloride of phosphorus employed must be free from pentachloride, but it is not necessary to attempt to free it from hydrochloric acid. During the latter portion of the

* Journal Chem. Soc., 1864, p. 225, and 1865, p. 1.

process it is desirable to break up the solid mass from time to time, in order that all parts of it may be exposed to the gaseous ammonia; and if this be properly done, the contents of the flask will be found to have increased in weight nearly, if not quite, 44 per cent.

The white amorphous powder produced by the action of water must be washed with cold water till the washings give no indication of a chloride, and then it is better to finish the washing with a little dilute alcohol.

The compound thus obtained is tasteless, but when moistened it reddens blue litmus paper, and it effervesces with solutions of alkaline carbonates. When suspended in solutions of metallic salts, it usually decomposes them, entering into combination with the metal, and that in the presence of the liberated acid. These salts, so easily formed, are all insoluble or very sparingly soluble in water, like the acid itself, even the salts of the alkalis. Another remarkable circumstance connected with this acid is, that it is capable of combining with 1, 2, 3, or 4 atoms of the base, according to the peculiarities of the metal itself, or the way in which it is presented.

This compound, though almost insoluble in water, is very slowly attacked by it, especially at a high temperature, with the production of pyrophosphodiamic acid. When boiled with dilute hydrochloric acid, it is speedily resolved into phosphoric acid and ammonia, pyrophosphodiamic acid being an intermediate product. When heated with strong sulphuric acid, it instantly dissolves, and this solution also contains pyrophosphodiamic acid.

The following analyses were made of different preparations of the substance dried at 100°C . :—

- I. 0.3315 grm. boiled with hydrochloric acid, and the ammonia determined in the usual manner, gave 1.243 grm. of ammonio-chloride of platinum.
- II. 0.197 grm. gave 0.755 grm. of ammonio-chloride of platinum.
- III. 0.197 grm. decomposed in the same way gave 0.247 grm. of pyrophosphate of magnesium.
- IV. 0.2595 grm. gave 0.987 grm. of ammonio-chloride of platinum.
- V. 0.2445 grm. gave 0.309 grm. of pyrophosphate of magnesium.
- VI. 0.1845 grm. regained from its ammonium salt, gave 0.705 grm. of ammonio-chloride of platinum.

VII. 0.225 grm. of substance regained from its combination with copper gave 0.2825 grm. of pyrophosphate of magnesium.

VIII. 0.320 grm. burnt with oxide of copper gave 0.114 grm. of water.

These numbers, when reckoned to 100 parts, give

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Phosphorus	—	—	35.02	—	35.29	—	35.38	—
Nitrogen	23.54	24.03	—	23.85	—	23.96	—	—
Hydrogen	—	—	—	—	—	—	—	3.93

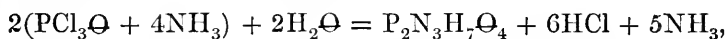
agreeing very closely with the numbers deduced from the formula $P_2N_3H_7O_4$.

	Calculated.	Mean of Analyses.
Phosphorus	62 35.43	35.23
Nitrogen	42 24.00	23.84
Hydrogen	7 4.00	3.93
Oxygen	64 36.57	—
	<hr/> 175 100.00	

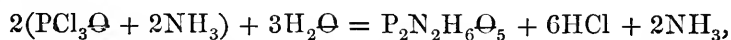
This may be viewed as the third member of the series of amides of pyrophosphoric acid, of which the first two have already been described by me; and it should by analogy be termed pyrophosphotriamic acid.

Pyrophosphoric acid	P_2	H_4O_7
Pyrophosphamic acid	$P_2NH_5O_6$ or $P_2(NH_2)H_3O_6$	
Pyrophosphodiamic acid	$P_2N_2H_6O_5$ or $P_22(NH_2)H_2O_5$	
Pyrophosphotriamic acid	$P_2N_3H_7O_4$ or $P_23(NH_2)H_1O_4$	

The reaction by which this substance is produced by the treatment of oxychloride of phosphorus with ammonia and water in succession may be briefly expressed thus:—



just as in the production of pyrophosphodiamic acid formerly described—



but in both cases there are intermediate products not recognized

in the above equations. I reserve the fuller consideration of what takes place when ammonia is passed over oxychloride of phosphorus till a future occasion.

SALTS.

If the rational formula of this acid be that above given, it might be expected that only one equivalent of hydrogen would be replaceable by a metal, or, in other words, that pyrophosphotriamic acid would be monobasic, just as the -diamic acid is bibasic, and the -amic acid is tribasic. The analysis of its salts shows indeed that such monobasic compounds are produced with the alkali-metals and many others, but it also shows that most metals are capable of displacing one or more equivalents of that hydrogen which we are apt to consider as more intimately associated with the nitrogen.

SILVER-SALTS.—*Monometallic.*—If a solution of nitrate of silver be added to an aqueous solution of pyrophosphotriamic acid, it gives a white gelatinous precipitate. But it is not easy to prepare in this way a quantity sufficient for analysis, and a portion so produced gave a determination of silver, which led to the conclusion that the salt was impure. A better method is to suspend the acid in cold water, and add a solution of nitrate of silver, when a flocculent precipitate subsides, and becomes granular. It is white, amorphous, and insoluble in water; dilute nitric acid or ammonia will dissolve out a little silver, and leave the pure monometallic salt. This salt is decomposed at once by hydrochloric acid; and this affords a ready means for its analysis, as the pyrophosphotriamic acid itself is converted on boiling into phosphoric acid and ammonia, which can be determined in the usual way.

The following determinations were obtained:—

- I. 0.259 grm. of silver-salt, washed with dilute ammonia, gave 0.133 grm. of chloride of silver, and 0.208 of pyrophosphate of magnesium.
- II. 0.241 grm. similarly washed gave 0.122 grm. of chloride of silver, and 0.581 grm. of ammonio-chloride of platinum.
- III. 0.298 grm. of salt, washed with dilute nitric acid, gave 0.1515 grm. of chloride of silver, and 0.235 grm. of pyrophosphate of magnesium.
- IV. 0.285 grm., similarly washed, gave 0.145 grm. of chloride of silver, and 0.679 grm. of ammonio-chloride of platinum.

This agrees closely with what ought to be obtained from a substance having the composition $P_2N_3H_6AgO_4$.

	Calculated.		I.	II.	III.	IV.
Phosphorus ..	62	21.98	22.42	—	22.01	—
Nitrogen	42	14.89	—	15.11	—	14.94
Hydrogen	6	2.13	—	—	—	—
Silver	108	38.30	38.61	38.09	38.26	38.29
Oxygen	64	22.70				
	<hr/>	<hr/>				
	282	100.00				

Trimetallic.—If a feebly ammoniacal solution of nitrate of silver be added to a solution of pyrophosphotriamic acid, there precipitates a yellowish salt. Or if the monometallic compound just described be treated with such an ammoniacal salt of silver in excess, it becomes of a bright yellow colour, heavy, granular, and easily washed by decantation. When dry it forms an orange-yellow powder. Dilute nitric acid, or ammonia, converts it at once into the white monometallic salt. Acetic acid attacks it but slowly, even when strong and at a boiling temperature. It was analysed by decomposition with hydrochloric acid.

I. 0.509 grm. of the yellow salt gave 0.442 grm. of chloride of silver, and 0.675 grm. of ammonio-chloride of platinum.

II. 0.5745 grm. gave 0.4995 grm. of chloride of silver, and 0.252 grm. of pyrophosphate of magnesium.

III. 0.286 grm. gave 0.2485 grm. of chloride of silver, and 0.3695 grm. of ammonio-chloride of platinum.

IV. 0.404 grm. gave 0.3515 grm. of chloride of silver, and 0.183 grm. of pyrophosphate of magnesium.

These numbers agree well with the composition $P_2N_3H_4Ag_3O_4$.

	Calculated.		Found.			
			I.	II.	III.	IV.
Phosphorus ..	62	12.50	—	12.25	—	12.65
Nitrogen	42	8.47	8.32	—	8.10	—
Hydrogen	4	0.81	—	—	—	—
Silver	324	65.32	65.34	65.46	65.39	65.48
Oxygen ..	64	12.90	—	—	—	—
	<hr/>	<hr/>				
	496	100.00				

These two silver-salts, white and yellow, and their ready convertibility into one another, afford a good test for pyrophosphotriamic acid.

BARIUM-SALTS.—*Monometallic.*—This salt was prepared by diffusing the acid through a solution of chloride of barium, and carefully neutralising the liberated hydrochloric acid by a few drops of ammonia. It was decomposed by hydrochloric acid, the different constituents being determined in the usual way.

I. 0.429 grm. gave 0.2045 grm. of sulphate of barium, and 1.1795 grm. of ammonio-chloride of platinum.

II. 0.3465 grm. gave 0.1665 grm. of sulphate of barium, and 0.3145 grm. of pyrophosphate of magnesium.

These numbers indicate the formula $P_2N_3H_6BaO_4$.

Calculated.			Found.	
			I.	II.
Phosphorus ..	62	25.56	—	25.34
Nitrogen	42	17.31	17.24	—
Hydrogen	6	2.47	—	—
Barium	68.6	28.28	28.06	28.27
Oxygen	64	26.38	—	—
<hr/>				
	242.6	100.00		

Dimetallic.—When pyrophosphotriamic acid was suspended in an excess of an ammoniacal solution of chloride of barium, it combined with twice as much of the metal.

The following analyses were made:—

I. 0.2335 grm. of salt gave 0.174 grm. of sulphate of barium, and 0.4895 grm. of ammonio-chloride of platinum.

II. 0.2445 grm. gave 0.1835 grm. of sulphate of barium, and 0.1793 grm. of pyrophosphate of magnesium.

These indicate the composition $P_2N_3H_5Ba_2O_4$.

Calculated.			Found.	
			I.	II.
Phosphorus ..	62	20.00	—	20.48
Nitrogen	42	13.54	13.14	—
Hydrogen	5	1.60	—	—
Barium	137.24	4.23	43.84	44.18
Oxygen	64	20.63	—	—
<hr/>				
	310.2			

LEAD-SALTS.—Lead is capable of entering into combination with pyrophosphotriamic acid in three different proportions.

Monometallic.—If the acid be treated with a solution of nitrate of lead, the result is a mixture of the compounds of 1 and 2 atoms of the metal. If, however, the solution be rendered decidedly acid with nitric acid, a pure mono-metallic salt may be produced. 0.203 grm. of the acid thus treated gave 0.327 grm. of salt, which indicates a compound of the formula $P_2N_3H_6PbO_4$. The excess of weight being due to the addition of lead, and the removal of a corresponding amount of hydrogen, gives the following percentage:—

	Calculated.	Found.
Lead ..	37.3 per cent.	38.1 per cent.

Dimetallic.—To produce this compound the acid was suspended in water, and an excess of a strong but slightly acid solution of acetate of lead was added. A dense white granular precipitate was the result. It was analysed in the usual way.

0.354 grm. of salt gave 0.2805 grm. of sulphate of lead, and 0.2035 grm. of pyrophosphate of magnesium.

This agrees sufficiently with the formula $P_2N_3H_5Pb_2O_4$.

		Calculated.	Found.
Phosphorus ..	62	16.32	16.05
Nitrogen	42	11.05	—
Hydrogen.....	5	1.32	—
Lead.....	207	54.47	53.95
Oxygen.....	64	16.84	—
		<hr/>	
		380	100.00

This compound is not turned yellow by iodide of potassium, except on the addition of hydrochloric acid.

Trimetallic.—When pyrophosphotriamic acid was warmed with basic acetate of lead, it combined with a larger portion of the metal. The following analyses were made:—

- I. 0.3405 grm. of salt gave 0.321 grm. of sulphate of lead, and 0.1535 of pyrophosphate of magnesium.

II. 0.2365 grm. gave 0.175 grm. of sulphide of lead, and 0.3165 grm. of ammonio-chloride of platinum.
This agrees with the formula $P_2N_3H_4Pb_3O_4$.

	Calculated.	Found.	
		I.	II.
Phosphorus ..	62	12.85	12.59
Nitrogen	42	8.70	—
Hydrogen	4	0.83	8.39
Lead	310.5	64.35	—
Oxygen	64	13.27	64.40
	—	—	64.08
	482.5	100.00	—

THALLIUM-SALT.—Pyrophosphotriamic acid treated with nitrate of thallium gives a heavy white compound, which is easily decomposed by rather strong nitric acid.

COPPER-SALTS.—Both neutral and ammoniacal salts of copper give up their metal to pyrophosphotriamic acid.

Monometallic.—The acid when treated with a solution of nitrate of copper to which some drops of nitric acid had been added, gave a pale blue compound. On analysis this was found to contain rather more copper than a pure monometallic salt should have done; but it consisted mainly, in all probability, of such a compound.

Dimetallic.—0.164 grm. of the acid, digested awhile with a solution of acetate of copper, gave a greenish salt, which, when dried at $100^{\circ}C$., weighed 0.215 grm. These numbers indicate that two equivalents of hydrogen had been replaced by copper, though perhaps the conversion had not been complete. The increased weight ought, by calculation, to have been 0.220.

If some of the acid be thrown into a solution of a copper-salt in excess of carbonate of ammonium, an effervescence takes place, and there results a green powder, insoluble in ammonia, but from which dilute acids dissolve out the copper.

I. 0.236 grm. of this salt gave 0.080 grm. of oxide of copper, and 0.646 grm. of ammonio-chloride of platinum.

II. 0.304 grm. gave 0.103 grm. of oxide of copper, and 0.285 grm. of pyrophosphate of magnesium.

This was certainly $P_2N_3H_5Cu_2O_4$.

		Calculated.		Found.	
				I.	II.
Phosphorus	62	26.25	—	26.18
Nitrogen	42	17.78	17.17	—
Hydrogen	5	2.12	—	—
Copper	63.2	26.76	27.04	27.03
Oxygen	64	27.09	—	—
		—	—	—	—
		236.2	100.00		

ZINC-SALT.—The acid decomposes chloride of zinc, forming a white pyrophosphotriamate.

CADMIUM-SALT.—It forms a white compound also, when treated with chloride of cadmium.

IRON-SALT.—*Monometallic.*—If the acid be digested with a solution of ferrous sulphate, a salt of a yellow-drab colour is produced, which resists the solvent power of dilute acids. 0.075 grm. of substance increased in this way to 0.089 grm., which points to the formula $P_2N_3H_6FeO_4$. The salt obtained ought to have weighed 0.086 grm.; but it probably contained a trace of ferric oxide mixed with the ferrous compound.

I have not succeeded in preparing any ferric pyrophosphotriamate, though the attempt has been made with ferric chloride, acetate, and ammonio-citrate. This is the more remarkable, as pyrophosphamic acid and phosphoric acid itself show such a readiness to combine with iron in that condition.

COBALT-SALT.—*Dimetallic.*—The acid, digested with a slightly ammoniacal solution of nitrate of cobalt, forms a compound of a beautiful violet colour, not decomposed by dilute hydrochloric, and but slowly by dilute sulphuric acid. 0.136 grm. gave thus 0.177 grm. of salt, which is sufficiently near to the theoretical amount to show that the composition was $P_2N_3H_5Co_2O_4$.

	Calculated.	By synthesis.
Cobalt ..	25.6 per cent.	24.3 per cent.

The same salt seems to be produced when the acid is treated with an ordinary solution of chloride of cobalt: but an analytical experiment gave also in this case less than the required percentage of metal.

NICKEL-SALT.—A feebly ammoniacal solution of sulphate of nickel gives a bright green pyrophosphotriamate.

MANGANESE-SALT.—Chloride of manganese gives a yellowish salt of this acid.

CHROMIUM-SALT.—A green compound may be produced by means of acetate of chromium.

MAGNESIUM-SALT.—This was produced by warming the acid with an ammoniacal solution of magnesia, and washing with water containing a little ammonia, and afterwards with pure water. On analysis, it appeared to be a mixture of monometallic and dimetallic salts.

POTASSIUM-SALT.—*Monometallic*.—Pyrophosphotriamic acid decomposes carbonate of potassium without dissolving. The white, almost insoluble salt is readily decomposed by acids. The following determinations were made:—

I. 0.312 grm. of salt gave 0.356 grm. of potassio-chloride of platinum.

II. 0.329 grm. gave 0.3402 grm. of pyrophosphate of magnesium.

III. 0.2985 grm. gave 0.3355 grm. of potassio-chloride of platinum.

This agrees with the numbers deduced from the formula $P_2N_3H_6K\bar{O}_4$.

	Calculated.		Found.		
			I.	II.	III.
Phosphorus ..	62	29.10	—	28.87	—
Nitrogen	42	19.72	—	—	—
Hydrogen	6	2.82	—	—	—
Potassium	39	18.31	18.17	—	17.95
Oxygen	64	30.05	—	—	—
	<hr/>	<hr/>			
	213	100.00			

AMMONIUM-SALT.—The acid forms a similar sparingly soluble ammonium-compound, which cakes together in small white lumps, and readily parts with the base when treated with dilute acids in the cold.

I. 0.129 grm. of salt gave 0.5945 grm. of ammonio-chloride of platinum.

II. 0.2095 grm. gave 0.9805 grm. of ammonio-chloride of platinum.

III. 0.3423 grm. gave 0.3995 grm. of pyrophosphate of magnesium.

IV. 0.220 grm. gave 1.014 grm. of ammonio-chloride of platinum.

This indicates the compound $P_2N_3H_6(NH_4)O_4$.

	Calculated.		Found.			
			I.	II.	III.	IV.
Phosphorus ..	62	32.29	—	—	32.61	—
Nitrogen	56	29.17	28.90	29.34	—	28.90
Hydrogen	10	5.21	—	—	—	—
Oxygen	64	33.33	—	—	—	—
	<hr/>	<hr/>				
	192	100.00				

MERCURY-SALT.—*Tetrametallic*.—It was observed early in the investigation that if pyrophosphotriamic acid be boiled with oxide of mercury, the oxide loses its colour and forms a white compound which is insoluble in dilute nitric or hydrochloric acid. This mercury-salt may be also prepared by diffusing the acid through a solution of corrosive sublimate, but Mr. Holmes seems always to have employed a slightly acid solution of the double chloride of mercury and ammonium. It is a heavy, white, granular powder, which becomes yellowish, and eventually dark-coloured, when exposed to light. Iodide of potassium first turns it scarlet, and then dissolves out the mercury. The following analyses were made:—

I. 0.4175 grm. of salt gave 0.3405 grm. of sulphide of mercury.

II. 0.5405 grm. gave 0.4405 grm. of sulphide of mercury.

III. 0.276 grm. gave 0.224 grm. of sulphide of mercury, and 0.3305 grm. of ammonio-chloride of platinum.

IV. 0.3415 grm. gave 0.277 grm. of sulphide of mercury, and 0.1305 grm. of pyrophosphate of magnesium.

These numbers require the formula $P_2N_3H_3Hg_4O_4$.

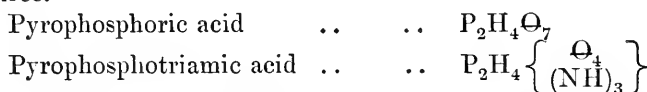
	Calculated.		Found.			
			I.	II.	III.	IV.
Phosphorus	62	10.86	—	—	—	10.67
Nitrogen	42	7.35	—	—	7.50	—
Hydrogen	3	0.53	—	—	—	—
Mercury	400	70.05	70.31	70.25	69.96	69.92
Oxygen	64	11.21	—	—	—	—
	<hr/>	<hr/>				
	571	100.00				

PLATINUM-SALT.—When pyrophosphotriamic acid is treated with a strong aqueous solution of platinic chloride, a bulky, yellowish compound is formed. This is entirely decomposed when washed with water, in presence of the liberated acid; but it may be safely washed with alcohol, and then water has not the same effect upon it. 0.097 grm. of the original acid gave 0.207 grm. of this platinum-compound, which shows that two equivalents of the metal must have entered into combination, displacing, no doubt, four equivalents of hydrogen; the formula being $P_2N_3H_3Pt''_2O_4$.

	Calculated.	Found.
Platinum ..	53.7 per cent.	54.1 per cent.

An attempt to prepare a salt of gold in a similar manner was unsuccessful.

The rational formula $P_2(NH_2)_3HO_4$ has been given above for this pyrophosphotriamic acid, but the elements are susceptible of another arrangement, which brings them more closely in accordance with the formula of pyrophosphoric acid, and indicates four equivalents of hydrogen as in a different position to the remaining three.



The following table exhibits at a glance the number of hydrogen atoms displaced by different metals, as far as the salts have been hitherto examined quantitatively:—

	1 eq.	2 eqs.	3 eqs.	4 eqs.
Ammonium.....	Yes	—	—	—
Potassium	Yes	—	—	—
Magnesium.....	?	?	—	—
Barium	Yes	Yes	—	—
Lead.....	Yes	Yes	Yes	—
Copper.....	?	Yes	—	—
Iron.....	Yes	—	—	—
Cobalt	—	Yes	—	—
Silver	Yes	—	Yes	—
Mercury	—	—	—	Yes
Platinum.....	—	—	—	Yes

II.—On the Action of Carbonic Oxide on Sodium-ethyl.

By J. ALFRED WANKLYN.

(Preliminary Notice.)

WHEN the compound containing sodium-ethyl and zinc-ethyl, which I have described on a former occasion,* is placed in contact with carbonic oxide, it becomes black. The darkening takes place slowly at ordinary temperatures, but very quickly, almost instantaneously, at temperatures approaching 100° C.

The black deposit is not carbonaceous, for it dissolves in hydrochloric acid. It is metallic, consisting of metallic zinc, and most probably also of metallic sodium. Absorption of the gas and formation of an oily product, accompany this deposit of metal.

The most convenient way of exhibiting the oil is to wash out with water the vessel in which the experiment has been performed, and then to distil the wash-water. The oil distils over with the first portions of the distillate.

In one experiment nearly 2 gramm. of oil were yielded by 1 gramm. of sodium employed in the state of sodium-ethyl. The oil was dried and rectified.

The greater portion boiled at about 105° C., and gave the following result on analysis:—

I. .2076 gramm. gave .5218 CO_2 and .2300 gramm. H_2O .

In another experiment a quantity of oil having about the same boiling point was obtained.

II. .1029 gramm. gave .2597 gramm. CO_2 , and .1155 gramm. H_2O .

The numbers approximate to those required by a compound containing one atom of carbonic oxide and two atoms of ethyl, $\text{CO}(\text{C}_2\text{H}_5)_2$.

	Calculated.		Found.	
			I.	II.
C_5	60	69.77	68.55	68.83
H_{10}	10	11.63	12.31	12.47
O	16	18.60	19.14	18.70
	<hr/>	<hr/>	<hr/>	<hr/>
	86	100.00	100.00	100.00

* Ann. Ch. Pharm. (1858) cviii., 67.

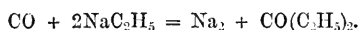
These details leave no doubt of the reaction which takes place between carbonic oxide and the compound containing sodium-ethyl. We have:—

(1) Disappearance of carbonic oxide.

(2) Precipitation of metal.

(3) Formation of an oil of pretty constant boiling-point, and commensurate in quantity with the sodium-ethyl taken, and approximating sufficiently in composition to $\text{CO}(\text{C}_2\text{H}_5)_2$.

Furthermore, the wash-water from which the oil distilled over was strongly alkaline. The reaction may, therefore, be represented by the equation:—



An experiment showed that zinc-ethyl alone is not attacked by carbonic oxide. The precipitation of zinc is obviously a secondary action. Sodium on being set free would instantly attack the zinc-ethyl, liberating zinc, and forming fresh sodium-ethyl.

The oil, $\text{CO}(\text{C}_2\text{H}_5)_2$, is probably identical with propione (ethyl-propionyl). I am at present engaged in preparing a quantity sufficient to admit of purification and of an examination of its physical properties and reactions. Among the latter I propose to study its oxidation products, and to inquire whether it is capable of uniting with hydrogen so as to form a pseudo-amylic alcohol. It may be remarked that it is by no means impossible that on adding water to the black mass containing finely divided metal saturated with the oil $\text{CO}(\text{C}_2\text{H}_5)_2$ addition of hydrogen may have taken place, and, indeed, both the boiling point of the oil and the analyses point in this direction.

Propione boils at 101°C .

Amylene-hydrate boils at 108°C .;

whilst our oil boiled at 105°C . The analytical numbers given by the oil are also intermediate between those required by propione and amylene-hydrate.

III.—*Note on the Constitution of Carbonic Oxide.*

By J. ALFRED WANKLYN.

THE general result of modern chemical research has been the addition of a new clause to Dalton's atomic theory. To the dictum "The elements consist of atoms of different weights, and the compounds are simple groupings of these atoms," we make this modern addition: An atom of an element is invariably combined with the same number of *equivalents*. The apparent contradictions of the law, which occur very frequently, are explained by self-saturation, more or less complete, as the case may be. In the compounds of hydrogen with carbon, which but a few years ago seemed to defy all attempts at classification, we have an admirable example of the working of the law. We find the utmost diversity in the ratio between the hydrogen and the carbon, but the *state of condensation* of each hydrocarbon always falls out so as to admit of the appropriate amount of self-saturation in every case; and, indeed, organic chemistry, as a whole, teaches this doctrine of uniform saturation. Inorganic chemistry, on the other hand, abounds in examples of failure of the law.

Proto- and per-salts of the metals (though these are easily explicable), ammonia and hydrochlorate of ammonia, the oxides of nitrogen, and oxide of carbon, are cited against the law.

In presence of these instances chemists take very different views.

One class of chemists abandon the greater part of the law, and insist only upon the declaration that the atoms of one set of elements combine with an even number of equivalents, whilst the atoms of the other set of elements combine with an uneven number of equivalents. These chemists are satisfied with very little predication in any given case, and yet have not disposed of all of the adverse cases, for the oxides of nitrogen do not fall under even this very limited statement of the law.

A second class of chemists take refuge in the possibility of there being two orders of chemical combination, the one *atomic*, the other mere *apposition*. In the hands of these chemists the law is in danger of being reduced to a mere figure of speech.

A third class abide by the law in its integrity, and look forward to an explanation of the inorganic difficulties.

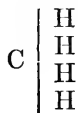
I have to offer an explanation of the anomaly which appears in the constitution of oxide of carbon. This compound contains only one atom of carbon in its molecule, and yet the one atom of carbon is united with only two equivalents of oxygen. It is unrepresented by either a hydrogen, or a chlorine, or even a sulphur analogue, for methylene, chloro-methylene, and proto-sulphide of carbon have not yet been obtained, though they have often been sought. This circumstance points to the oxygen as the source of the irregularity. Let us put 8 for the atomic weight of oxygen, and let the atom of oxygen be capable of saturating two atoms of hydrogen, and the difficulty with regard to carbonic oxide vanishes.

$$O'' = 8.$$

Marsh Gas.

Carbonic Oxide.

Carbonic Acid.



This being so, the usual oxygen-compounds such as water, carbonic acid, the common oxides of the metals will contain oxygen in its second state of condensation. Now, there is no reason for believing that the commonest state of combination of oxygen, or any other polyatomic element, is of necessity its simplest state. The compounds of carbon have taught us how very common and stable a complex grouping of an element may be; and too little is known about the various states of condensation of carbon, to admit of our attaching much weight to the circumstance that compounds containing only 8 of oxygen in the molecule are as yet unrecognised; and, moreover, Rose's quadrantoxides appear to offer examples of the occurrence of this simple oxygen-atom in the uncondensed state. How, for example, is the quadrantoxide of the monatomic metal, silver (containing 4 of oxygen to 108 of silver) to be explained, if the atomic weight of oxygen be not 8?

I will conclude with suggesting a nomenclature and a notation to express the different states of condensation of a given element, taking carbon as the example. The carbon of marsh-gas I propose to call "one-fold carbon," or carbon simplex (symbol C). The carbon of alcohol and acetic acid, two-fold carbon, or carbon duplex (symbol C'); the carbon of glycerin, three-fold

carbon," or carbon triplex (symbol C), &c.; and carbon multiplex is a general expression for all but carbon simplex.

The following are examples of this notation (I have taken oxygen simplex $\text{O}''=8$):—

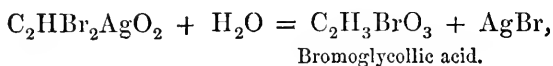
Alcohol	$\text{C}\text{H}_6\text{O}$
Methylic Ether.....	$\text{C}_2\text{H}_6\text{O}$
Tetrylic Alcohol	$\text{C}\text{H}_{10}\text{O}$
Common Ether	$\text{C}_2\text{H}_{10}\text{O}$

IV.—On the Constitution of some Carbon-compounds.

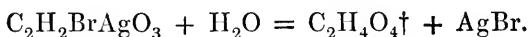
By HENRY DEBUS, Ph.D, F.R.S.

Part I.

THE silver-salt of dibromosuccinic acid decomposes, according to Messrs. Perkin and Duppá,* under the influence of heat, and forms argentic bromide and bromoglycollic acid. The silver-compound of the latter produces, under similar conditions, argentic bromide, and an acid the composition of which is supposed to be represented by the formula $\text{C}_2\text{H}_4\text{O}_4$. These chemical changes may be represented by the following equations:—



and



The conversion of dibromosuccinic acid into tartaric or racemic acid takes place by similar reactions.

It appears that Messrs. Perkin and Duppá adopted the formula $\text{C}_2\text{H}_4\text{O}_4$ for their new acid without experimental verification, because, in many instances, organic bodies exchange one atom of chlorine or bromine for the elements HO. I am not aware, indeed, that the acid or any of its salts have been analysed. It is, however, well-known that organic bodies may also lose their chlorine

* Chem. Soc. Qu. J. xii., 5.

† The acid $\text{C}_2\text{H}_4\text{O}_4$ may be regarded as standing to the hypothetical glycerin, $\text{C}_2\text{H}_6\text{O}_3$, in the same relation as glyceric acid does to common glycerin.

or bromine according to other modes than the one indicated by the above equations. Ethylenic chloride boiled with an alcoholic solution of potash, loses the elements HCl ; dibromopyrotartaric acid yields with caustic soda, aconic acid, sodic bromide and water; and a similar mode of decomposition is exhibited by the bromine-compound of milk-sugar, by dichlorhydrin and trichlorhydrin. The silver-salt of bromoglycollic acid might undergo a similar change and furnish the acid $\text{C}_2\text{H}_2\text{O}_3$ and argentic bromide. The formula $\text{C}_2\text{H}_2\text{O}_3$ belongs to glyoxylic acid, formed by the action of nitric acid on common alcohol.

I proposed to myself the following questions:—

(1) Which of the two formulae $\text{C}_2\text{H}_2\text{O}_3$ and $\text{C}_2\text{H}_4\text{O}_4$ belongs to the acid obtained by Messrs. Perkin and Duppa from dibromacetic acid.

(2) In case the composition of this acid is represented by $\text{C}_2\text{H}_2\text{O}_3$, is it identical or isomeric with glyoxylic acid?

These questions appeared to me to possess considerable theoretical interest, in consequence of considerations which will be described in this paper.

I have to thank my friend Mr. Duppa for the dibromacetic acid employed in the following experiments:—

A quantity of dibromacetic acid, which boiled at about 225°C ., was diluted with water, neutralised with calcic carbonate at ordinary temperatures, and the lime-salt was precipitated with argentic nitrate. The white crystalline precipitate, after previous washing with cold water, was boiled for some minutes with water. It decomposed easily into argentic bromide and an acid which remained dissolved in the liquid. The argentic bromide was separated by means of a filter, and the filtrate neutralised with argentic oxide. The silver-compound thus obtained decomposed at the temperature of boiling water, producing, as in the former case, argentic bromide and a soluble acid. The clear acid liquid dissolved marble with effervescence, and gave, after neutralisation and suitable concentration, a crop of small prismatic crystals. The latter were placed in hot water in such quantities that a saturated solution was formed, and on allowing this solution to cool, the crystals were again obtained in a pure state.

These crystals were carefully compared with glyoxylate of lime (prepared from alcohol) and found to agree perfectly with the latter in form, solubility, and reactions. Their aqueous solution gave a white precipitate with lime-water, which precipitate, dis-

solved in acetic acid immediately after its formation, but lost its solubility in that acid after it had been kept for some time, or after exposure to a temperature of 100° C. The precipitate produced by lime-water in calcic glyoxylate decomposes at 100° into oxalate and calcic glycolate. Zinc acetate and plumbic acetate gave white crystalline precipitates, but plumbic nitrate and argentic nitrate failed to produce any change in the aqueous solution. Every reaction was made twice, once with the salt from dibromacetic acid, and the second time with calcic glyoxylate from alcohol, and in each instance both salts behaved exactly in the same manner.

The experiments made to determine the solubility of the substance in water gave the following results:—

(a) 7.371 grms. solution of the salt made from dibromacetic acid gave, after evaporation at 100° C, 0.053 grm. solid residue.

(b) 4.97 grms. solution of the lime-salt made from alcohol gave, after evaporation at 100° C., 0.0355 grm. residue.

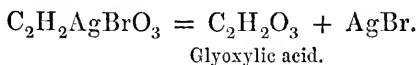
The solutions had been prepared at the same time, and under precisely the same conditions, at a temperature of 18° C.

100 parts of water dissolve therefore

of substance (a) 0.719 grm.

of substance (b) 0.714 grm.

According to these results, I believe I am justified in assuming that the acid prepared from dibromacetic acid is identical with glyoxylic acid prepared by the oxidation of common alcohol. The formula of the latter is $C_2H_2O_3$, and therefore the decomposition of the silver-salt of bromo-glycollic acid may be represented thus:—



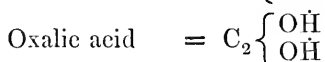
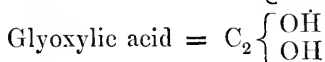
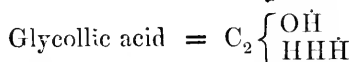
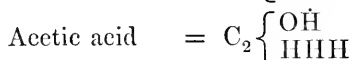
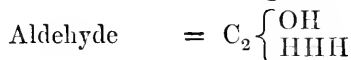
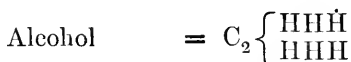
If we consider the compounds which are derived from ethylic hydride by the gradual addition of oxygen to the latter, our attention is in the first instance arrested by the fact that each mode of reaction takes place twice.

If ethylic hydride is represented by the formula



and if \bar{H} denotes one atom of hydrogen and one of oxygen, both

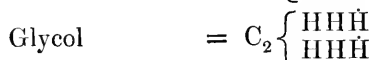
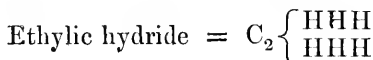
of the same chemical value which attaches to them in the ordinary water-type, where they are written separately by the side of the radical which stands for a second atom of hydrogen, and so completes the molecule, then the oxygen-compounds in question may be represented by the following series :—



The changes of the group $\text{C}_2 \left\{ \begin{array}{c} \text{H}_3 \\ \text{H}_3 \end{array} \right.$ are therefore the following :
 (1). Addition of one atom of oxygen ; (2). Loss of two atoms of hydrogen ; (3). Combination with one atom of oxygen, the products of the reactions being alcohol, aldehyde and acetic acid. The repetition of these processes produces glycollic acid, glyoxylic acid, and oxalic acid.

Instead of allowing these changes to take place in succession, we may consider them to take place simultaneously ; we may add, at once, two atoms of oxygen to ethylic hydride ; and instead of subtracting twice each time two atoms of hydrogen, we may at once remove four atoms of this element, and finally add two atoms of oxygen to the residue.

In this manner we arrive at the following compounds :—



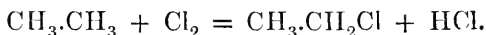
and herewith the list of the oxygen derivatives of ethylic hydride is complete.

It is worthy of notice that the successive steps from ethylic hydride to oxalic acid, as represented in the foregoing tables, show that the six atoms of hydrogen in the ethylic hydride arrange themselves in two groups, each group containing three atoms of the element and undergoing the same transformations. The introduction of oxygen and the removal of hydrogen follows a certain rule, which must be dependent on the constitution of ethylic hydride and the nature of oxygen. The most simple view of the constitution of ethylic hydride, in accordance with the above facts, follows from the following considerations.

Modern chemistry assumes that chemical reactions take place between molecules; the determination of the molecular weight of bodies is therefore one of the most important problems of the science. The molecular weight of marsh gas is represented by the formula CH_4 . Instead, as is commonly done, of contemplating compound bodies as originating by union of their atoms, we adopt the opposite method and consider them to be derived from a series of molecules. A molecule may be looked upon as a system of atoms governed by certain forces, which system must be in a state of equilibrium if no external influences produce a disturbing effect. If such a molecule is approached by a second molecule, one of the following effects may take place. Either the two molecules simply unite and form one new molecule, or, as a consequence of action and reaction, two or more new molecules result. Examples of the first kind are the formation of chloride of ammonium from hydrochloric acid and ammonia, the double salt of bichloride of platinum and chloride of potassium, the combinations of water with many salts and other similar cases. The second mode of action may be exemplified by the formation of acetamide and hydrochloric acid from chloride of acetyl and ammonia. If we imagine one atom of hydrogen to be removed from the molecule of marsh-gas, it appears, as a natural consequence, that the equilibrium between the atoms of the molecule must be destroyed, and that a resultant of given magnitude and direction must originate. The same process may be conceived with a second molecule of marsh-gas, and a similar resultant must be obtained. If, now, the two residues of marsh-gas are placed together, so that these two equal resultants counteract each other, a stable molecule must be obtained. This is commonly expressed by saying that an atom

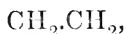
of methyl has replaced an atom of hydrogen in marsh-gas, and that this atom of methyl plays the part of an atom of hydrogen.

Ethylic hydride would, according to the above considerations, be composed of the two residues CH_3 and CH_3 of marsh-gas; it would be identical with methyl. Schorlemmer has prepared ethylic chloride from methyl, and thus the above view appears to be confirmed.

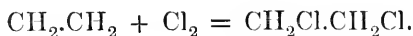


Ethylic chloride.

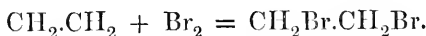
The compound molecule ethylic hydride (or methyl) which consists of the two residues CH_3 and CH_3 can evidently not remain in equilibrium if from one or the other residue an atom of hydrogen is withdrawn, just as some forces which are around a given point in equilibrium cannot remain so if we suppose one of the forces to be removed. If, however, of these forces two are equal and act in opposite directions, both may be removed from the point without disturbing the equilibrium of the remaining forces. In a similar manner, a stable molecule may be derived from ethylic hydride, if each of the residues of which it is composed loses one atom of hydrogen. Thus we obtain



or ethylene. The two chemical units which have thus been removed from ethylic hydride in order to obtain ethylene may be added again, and therefore we say that ethylene is diatomic. It is not necessary that these two units should be hydrogen, they may be chlorine or bromine, forming chloride or bromide of ethylene.

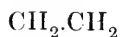


Chloride of ethylene.



Bromide of ethylene.

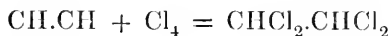
Each of the two marsh-gas residues present in ethylene may lose an atom of hydrogen, and thus the stable molecule of acetylene results, which, because four units may be added to it, is tetratomic.



Ethylene.



Acetylene.



Acetylene.

Chloride of acetylene.

The view on which the foregoing considerations are based leads to the conclusion that CH_3 and CH_3 in ethylic hydride, CH_2 and CH_2 in ethylene, and CH and CH in acetylene, are the proximate constituents of the molecules of these bodies. It is apparent that when oxygen is introduced into the molecule of ethylic hydride, the hydrogen ought to comport itself as if it were arranged in two groups; each consisting of three atoms, and each change produced in the molecule ought to take place twice. Three couples of bodies are thus produced, the members of each couple possessing similar chemical properties.

Alcohol	$\text{CH}_3.\text{CH}_2\dot{\text{H}}$; $\text{CH}_2\dot{\text{H}}.\text{CO}\dot{\text{H}}$	Glycollic acid
Aldehyde	$\text{CH}_3.\text{CO}\dot{\text{H}}$; $\text{CO}\dot{\text{H}}.\text{CO}\dot{\text{H}}$	Glyoxylic acid
Acetic acid	$\text{CH}_3.\text{CO}\dot{\text{H}}$; $\text{CO}\dot{\text{H}}.\text{CO}\dot{\text{H}}$	Oxalic acid

Perkin and Kekulé have called attention to the alcoholic properties of glycollic acid. I have shown that glyoxylic acid possesses the characteristic properties of an aldehyde, and the relation of oxalic to acetic acid is self-evident from the above table. The properties of alcohol, aldehyde, and acetic acid are dependent on the change which the group CH_3 has undergone; it shows alcoholic properties when it has become $\text{CH}_2\dot{\text{H}}$,—the properties of aldehyde in the state of $\text{CO}\dot{\text{H}}$,—and of acid when it has been transformed into $\text{CO}\dot{\text{H}}$; and because the group CH_3 occurs twice in ethylic hydride, therefore two bodies with alcoholic properties, two aldehydes, and two acids may be derived from it.

If the changes which the two groups CH_3 , CH_3 may undergo in succession in ethylic hydride take place simultaneously in both residues, the following bodies result:—

Ethylic hydride	$\text{CH}_3.\text{CH}_3$
Glycol	$\text{CH}_2.\dot{\text{H}}\text{CH}_2\dot{\text{H}}$
Glyoxal	$\text{CO}\dot{\text{H}}.\text{CO}\dot{\text{H}}$
Oxalic acid	$\text{CO}\dot{\text{H}}.\text{CO}\dot{\text{H}}$

In the former cases the derivatives of the two groups CH_3 , CH_3

were in each substance not the same; in glycollic acid, $\text{CH}_2\dot{\text{H}}.\text{CO}\dot{\text{H}}$; for example, one of the residues, $\text{CO}\dot{\text{H}}$, contributes the acid, and the other, $\text{CH}_2\dot{\text{H}}$, the alcoholic properties; whereas in the cases mentioned in the last table, the derivatives of the two residues CH_3 , CH_3 are in exactly the same condition, and therefore we have, so to say, a double alcohol, a double aldehyde, and a double acid, viz., glycol, glyoxal, and oxalic acid.

From considerations of a similar nature to those hitherto employed, it is easy to foresee the probable existence of the body $\text{CH}_2\dot{\text{H}}.\text{CO}\dot{\text{H}}$, a substance which would possess the composition of acetic acid, but the properties of alcohol and aldehyde, and would stand to glycollic acid in the same relation as common aldehyde to acetic acid.

From the point of view here adopted it is also easy to recognise why cyanide of methyl and the nitrile of acetic acid must be identical.

CH_3CH_3	Ethylic hydride.
$\text{CH}_3\text{CO}\dot{\text{H}}$	Acetic acid.
$\text{CH}_3.\text{CN}$	Nitrile of acetic acid—cyanide of methyl.

With regard to the bodies which may be looked upon as derivatives of ethylic hydride and chlorine, it is at once seen that there must be at least two isomeric series of chlorinated bodies. Hydrogen may be replaced in CH_3 , CH_3 atom after atom, first in one group, CH_3 , and then in the other. Or the substitutions may proceed in both groups at once. The following table represents the two modes of substitution:—

Ethylic chloride	$\text{CH}_3.\text{CH}_2\text{Cl}$	1	$\text{CH}_3.\text{CH}_2\text{Cl}$	Ethylic chloride
	$\text{CH}_3.\text{CHCl}_2$	2	$\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$	Chloride of ethylene
	$\text{CH}_3.\text{CCl}_3$	3	$\text{CH}_2\text{Cl}.\text{CHCl}_2$	
	$\text{CH}_2\text{Cl}.\text{CCl}_3$	4	$\text{CHCl}_2.\text{CHCl}_2$	
	$\text{CHCl}_2.\text{CCl}_3$	5	$\text{CHCl}_2.\text{CCl}_3$	
	$\text{CCl}_3.\text{CCl}_3$	6	$\text{CCl}_3.\text{CCl}_3$	

Theory asserts that if all the hydrogen atoms in CH_3 , CH_3 are of the same chemical value, the formulæ $\text{C}_2\text{H}_5\text{Cl}$, C_2HCl_5 , and C_2Cl_6 represent only one compound, while the formulæ $\text{C}_2\text{H}_4\text{Cl}_2$, $\text{C}_2\text{H}_3\text{Cl}_3$, and $\text{C}_2\text{H}_2\text{Cl}_4$, on the other hand, represent each two compounds. C_2HCl_5 , prepared by the action of chlorine on chloride of ethyl, seems indeed to be identical with the body

C_2HCl_5 from chloride of ethylene. The chlorinated chloride of ethylene boils at 154° , and has a specific gravity of 1.662; the isomeric body from chloride of ethyl was not obtained quite pure, and in this impure state was found to boil at 146° , and to have the specific gravity 1.644. And inasmuch as they appear to comport themselves in the same manner with alcoholic potash-solution, I think these bodies may be considered to be identical.

Hübner* asserts the existence of three bodies of the formula $C_2H_3Cl_3$. Two are the well-known derivatives of chloride of ethyl and chloride of ethylene, and the third was obtained by him from pentachloride of phosphorus and chloride of acetyl. The existence of this third chloride of the formula $C_2H_3Cl_3$ is, however, very doubtful, because Hübner obtained by accident only one drop of it, which *appeared* to boil at 60° , and just served for one chlorine determination. Such evidence does not appear to me to be sufficient for the admission of new bodies into the scientific system.

The constitution which has been adopted for ethylic hydride and its derivatives in these pages is also confirmed by the synthesis of acetic acid from cyanide of methyl, or from potassium-methyl and carbonic acid. The same theory explains also why the products of the decomposition of chloride of ethylene by caustic potash are identical with those obtained by the action of caustic potash on chloride of ethylidene. The chloride of ethylene may be represented by $CH_2Cl.CH_2Cl$, the chloride of ethylidene by $CH_3.CHCl_2$. The results of their decomposition by caustic potash are water, chloride of potassium, and chloride of vinyl, C_2H_3Cl . The latter therefore originates by the subtraction of HCl from the organic chlorides. But whether we take HCl from $CH_2Cl.CH_2Cl$ or from $CH_3.CHCl_2$ the result must in both cases be the same, viz., $CH_2.CHCl$.

We assume that if an organic body loses chemical units, such units cannot be taken out of the same carbon group which forms one of the proximate constituents of the body, but are supplied by different carbon groups, of which the body happens to be composed.

If, for example, ethylic hydride, by the removal of two atoms of hydrogen, is to be converted into ethylene, or the latter into acetylene, each of the residues CH_3 in $CH_3.CH_3$ must lose 1 at. of hydrogen. Thus $CH_3.CH_3$ would become $CH_2.CH_2$, or $CH.CH$

* Ann. Ch. Pharm. cxx., 330.

respectively, and not CHCH_3 , or C_2CH_2 . This view is supported by the fact that hitherto the attempts to prepare methylene CH_2 have been unsuccessful, and that bodies of the molecular weights, CH and CH_3 , are unknown.

It also appears worthy of notice that the glycol of the methylic, and the glycerin of the ethylic series, are still unknown. The experiments of Butlerow and of Simpson,* undertaken with the desire to obtain these bodies, are known to chemists. If the glycol of the methyl series existed, its formula would be $\left. \begin{smallmatrix} \text{CH}_2 \\ \text{H}_2 \end{smallmatrix} \right\} \text{O}_2$, or $\text{CH}_2\ddot{\text{H}}\ddot{\text{H}}$. As soon as we attempt to replace the iodine in CH_2I_2 , by $\ddot{\text{H}}\ddot{\text{H}}$ water is eliminated, and dimethylenic oxide $\text{C}_2\text{H}_4\text{O}_2$ is produced. It would, therefore, appear as if the group $\ddot{\text{H}}$ could not exist twice in combination with 1 at. of carbon. If this is the case, the failure of the experiments to obtain the glycerin of the ethyl-series is explained. Ethylic hydride contains only two atoms of carbon, and therefore the group $\ddot{\text{H}}$ can only be introduced twice into the place of hydrogen. Propylic hydride contains 3 atoms of carbon, and accordingly in glycerin, which may be considered as a derivative of propylic hydride, we have $3\ddot{\text{H}}$; and as a further confirmation, we find the first tetratomic alcohol to contain four atoms of carbon.

The following table contains the formulæ of the alcohols derived from some of the hydrocarbon-compounds of the series $\text{C}_n\text{H}_{2n+2}$:—

Methylic series.	Ethylic series.	Propylic series.	Butylic series.
$\text{CH}_3\ddot{\text{H}}$	$\text{C}_2\text{H}_5\ddot{\text{H}}$	$\text{C}_3\text{H}_7\ddot{\text{H}}$	$\text{C}_4\text{H}_9\ddot{\text{H}}$
	$\text{C}_2\text{H}_4\ddot{\text{H}}\ddot{\text{H}}$	$\text{C}_3\text{H}_6\ddot{\text{H}}\ddot{\text{H}}$	$\text{C}_4\text{H}_8\ddot{\text{H}}\ddot{\text{H}}$
		$\text{C}_3\text{H}_5\ddot{\text{H}}\ddot{\text{H}}\ddot{\text{H}}$	
			$\text{C}_4\text{H}_6\ddot{\text{H}}\ddot{\text{H}}\ddot{\text{H}}\ddot{\text{H}}$

We perceive by this table that in no compound does the number of the groups $\ddot{\text{H}}$ exceed those of the carbon-atoms. I believe this rule holds good in all native compounds.

Not long ago Carius† described as propyl-phycite a body which had been prepared from epichlorhydrin, and to which he gives the formula $\left. \begin{smallmatrix} \text{C}_3\text{H}_4 \\ \text{H}_4 \end{smallmatrix} \right\} \text{O}_4$. This body would form an excep-

* Jahresbericht, 1857, 461. Ann. Ch. Pharm. cvii., 110; cxi., 242; cxiv., 204; cxv 322.

† Ann. Ch. Pharm. cxxxiv., 71.

tion to what appears in the above and many other examples, as a rule. The propyl-phycite is, however, described as an amorphous, viscous mass, and the same properties belong to its derivatives.

Even if it were possible to obtain such bodies in a sufficiently pure state for analysis, it might still be doubted whether the formula $\left. \begin{smallmatrix} \text{C}_3\text{H}_4 \\ \text{H}_4 \end{smallmatrix} \right\} \text{O}_4$ was the correct representation of the composition of the propyl-phycite, because it may have been, in the state in which it was analysed, a hydrate. Pseudopropylic alcohol forms hydrates with a definite boiling point.

Carius has, however, prepared, by the action of sodium-alcoholate on dichlorobromhydrin, two bodies, which he considers to be the ethers of the propyl-phycite $\left. \begin{smallmatrix} \text{C}_3\text{H}_4 \\ \text{H} \end{smallmatrix} \right\} \text{O}_4$ and $\left. \begin{smallmatrix} \text{C}_3\text{H}_4 \\ (\text{C}_2\text{H}_5)_4 \end{smallmatrix} \right\} \text{O}_4$. From these bodies we cannot deduce the formula of the corresponding alcohol.

Williamson and Kay* obtained from chloroform and sodium-alcoholate, a substance which may be regarded as the ether of methyl-glycerin $\left. \begin{smallmatrix} \text{CH}''' \\ (\text{C}_2\text{H}_5)_3 \end{smallmatrix} \right\} \text{O}_3$, and Mr. Bassett† has prepared from chloropicrin, orthocarbonate of ethyl $\left. \begin{smallmatrix} \text{Civ} \\ (\text{C}_2\text{H}_5)_4 \end{smallmatrix} \right\} \text{O}_4$. The corresponding hydrogen-compounds, however, cannot be obtained from these ethers.

Another circumstance deserves attention. Carius could not replace more than two hydrogen-atoms in propyl-phycite by acid radicals. The treatment of dichlorobromhydrin, $\text{C}_3\text{H}_4 \cdot \text{H} \cdot \text{Cl}_2 \cdot \text{Br}$, with sodic acetate and acetic acid failed to produce the ether $\left. \begin{smallmatrix} \text{C}_3\text{H}_4 \\ (\text{C}_2\text{H}_3\text{O})_4 \end{smallmatrix} \right\} \text{O}_4$ but gave instead a number of substances, which must be regarded as the result of a very complicated reaction.

From the above it will be seen that our knowledge of the propyl-phycite is still very incomplete, and that its formula has not been established on a satisfactory basis. If we consider it as a hydrate of the formula $\left. \begin{smallmatrix} \text{C}_3\text{H}_3 \\ \text{H}_3 \end{smallmatrix} \right\} \text{O}_3, \text{H}_2\text{O}$, the rule which obtains with regard to other artificial and natural alcohols would also apply to the propyl-phycite.

The rule which asserts that the atomicity with regard to the

group $\dot{\text{H}}$ of a carbon-compound cannot be greater than the number of carbon-atoms present, holds good also for the acids. The methyl-series contains only monoatomic acids, for the body, $\text{CO}\dot{\text{H}}\dot{\text{H}}$ is unknown. The ethyl-series contains diatomic, but no undoubted triatomic acid; whereas in the propyl-series glyceric acid is certainly triatomic, &c., &c.

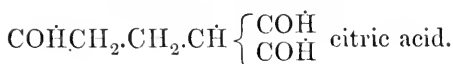
The view adopted in the present paper assumes that all the hydrocarbons of the general formula $\text{C}_n\text{H}_{2n+2}$ consist of as many residues of marsh-gas molecules as there are carbon-atoms in the compound, or, in other words, contain these residues as their proximate constituents. The alcohols, aldehydes, and acids of these carbon and hydrogen compounds are produced by the substitution of oxygen, or $\dot{\text{H}}$, or of oxygen and $\dot{\text{H}}$ for hydrogen.

If we compare the formulæ of formic acid, acetic acid, and oxalic acid,

Formic acid	$\text{H.CO}\dot{\text{H}}$
Acetic acid	$\text{CH}_3.\text{CO}\dot{\text{H}}$
Oxalic acid	$\text{CO}\dot{\text{H}}.\text{CO}\dot{\text{H}}$

it appears that the basicity of an acid is equal to the number of times the group $\text{CO}\dot{\text{H}}$ occurs in it. I think this rule applies to all organic acids derived from the hydrocarbons $\text{C}_n\text{H}_{2n+2}$. Thus propionic acid $\text{CH}_3.\text{CH}_2.\text{CO}\dot{\text{H}}$ is monobasic; malonic acid $\text{CO}\dot{\text{H}}.\text{CH}_2.\text{CO}\dot{\text{H}}$ bibasic; mesoxalic acid $\text{CO}\dot{\text{H}}.\text{CO}.\text{CO}\dot{\text{H}}$ bibasic; tartaric acid $\text{CO}\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{CO}\dot{\text{H}}$, bibasic and tetratomic. The group $\text{CO}\dot{\text{H}}$ is derived from CH_3 , and, therefore, a tribasic acid must be derived from a hydrocarbon-compound in which the group CH_3 occurs three times. Propylic hydride is $\text{CH}_3.\text{CH}_2.\text{CH}_3$, and therefore no tribasic acid can occur in the propylic series.

Citric acid is a tribasic acid, and its corresponding hydrocarbon is represented by the formula C_6H_{14} . This hydrocarbon could be derived from six molecules of marsh-gas. The first five molecules would produce $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_3$. In order to obtain 3CH_3 in C_6H_{14} , the sixth molecule CH_4 must attach itself, not to one of the two CH_3 , but to one of the residues represented by CH_2 . Thus, because the residue and the marsh-gas molecule must each lose one atom of hydrogen, we obtain $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH} \begin{Bmatrix} \text{CH}_3 \\ \text{CH}_3 \end{Bmatrix}$ and by substitution

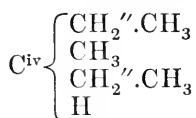


Black oxide of manganese oxidises the three groups $\text{CO}\ddot{\text{H}}$, and the residue $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}$ takes up one atom of H and forms acetone.

Tribasic acids, which may be considered as derived from one of the hydrocarbons $\text{C}_n\text{H}_{2n+2}$, must contain the residue CH or C amongst their proximate constituents.

The rational formula of propylic hydride is $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3$, or $\underbrace{\text{CH}_3\cdot\text{CH}_3}_{\text{CH}_2}$ If in each of the residues 1 at. of hydrogen is replaced

by cyanogen, we obtain $\underbrace{\text{CH}_2\text{Cy}\cdot\text{CH}_2\text{Cy}}_{\text{CHCy}}$; and replacing the nitrogen of the cyanogen by $\text{O}\ddot{\text{H}}$ we have $\text{CO}\ddot{\text{H}}\cdot\text{CH}_2\text{CH}\cdot\text{CO}\ddot{\text{H}}$, $\text{CH}_2\text{CO}\ddot{\text{H}} = \text{carballylic acid.}^*$ The corresponding hydrocarbon of carballylic acid would be $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3$, or according to one of the more common expressions,



The atomicity of an acid or an alcohol depends on the number of times the group $\ddot{\text{H}}$ is contained in it. Tartaric acid contains 6 atoms of oxygen, 6 atoms of hydrogen, and 4 of carbon, which elements, according to the chemical properties of tartaric acid, must be arranged in the following manner: $\text{CO}\ddot{\text{H}}\cdot\text{CH}\ddot{\text{H}}\cdot\text{CH}\ddot{\text{H}}\cdot\text{CO}\ddot{\text{H}}$; and in an analogous manner, succinic acid = $\text{CO}\ddot{\text{H}}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\ddot{\text{H}}$, and malic acid = $\text{CO}\ddot{\text{H}}\cdot\text{CH}\ddot{\text{H}}\cdot\text{CH}_2\cdot\text{CO}\ddot{\text{H}}$. Succinic acid may be prepared from butyric acid, the latter from butylic alcohol, and butylic alcohol from butylic hydride. Thus we have the following series:—

$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$	Butylic hydride
$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\ddot{\text{H}}$	Butylic alcohol
$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\ddot{\text{H}}$	Butyric acid
$\text{CH}_2\ddot{\text{H}}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\ddot{\text{H}}$	
$\text{CO}\ddot{\text{H}}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\ddot{\text{H}}$	Succinic acid
$\text{CO}\ddot{\text{H}}\cdot\text{CH}\cdot\ddot{\text{H}}\cdot\text{CH}_2\cdot\text{CO}\ddot{\text{H}}$	Malic acid
$\text{CO}\ddot{\text{H}}\cdot\text{CH}\ddot{\text{H}}\cdot\text{CH}\cdot\ddot{\text{H}}\cdot\text{CO}\ddot{\text{H}}$	Tartaric acid

* Simpson. Proceedings of the Roy. Soc. xii., 236.

The manner in which the proximate constituents of butylic hydride become changed, in consequence of the gradual introduction of oxygen into its molecule, is clearly perceptible in the above table. The question very naturally arises, can the second atom of hydrogen in the residues $\dots \text{CH}\dot{\text{H}}.\text{CH}\dot{\text{H}}, \dots$ be replaced by $\dot{\text{H}}$ and the bodies $\text{CO}\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{CO}\dot{\text{H}} = \text{C}_4\text{H}_6\text{O}_8$ and $\text{CO}\dot{\text{H}}.\text{CH}\dot{\text{H}}, \text{CH}\dot{\text{H}}.\text{CO}\dot{\text{H}} = \text{C}_4\text{H}_6\text{O}_7$ be obtained?

According to our present experience, it appears that this cannot be done. Tartaric acid is hardly attacked by chlorine, and nitric acid removes one of the groups $\text{CH}\dot{\text{H}}$ altogether, and produces tartronic acid $\text{CO}\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{CO}\dot{\text{H}} = \text{C}_3\text{H}_4\text{O}_5$. Also, tartronic acid is not succeeded by an acid wherein two atoms of oxygen have joined the group CH_2 . The composition of such an acid would be $= \text{CO}\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{CO}\dot{\text{H}} = \text{C}_3\text{H}_4\text{O}_6$. The ammonia-salt of mesoxalic acid is $= \text{C}_3(\text{NH}_4)_2\text{O}_5$. The relations of this acid to various members of the uric acid series also tend to establish the formula $\text{C}_3\text{H}_2\text{O}_5$. Therefore we pass from tartronic acid to mesoxalic acid by the addition of 1 at. O. to the group $\text{CH}\dot{\text{H}}$, and the subtraction of H_2O .



The latter may be converted into tartronic acid by means of sodium-amalgam.

The properties of the group CH_2 , as exhibited in the above examples, occur again in many other cases.

V.—On the Expansion of Water.

By A. MATTHIESSEN, F.R.S.

[Abstract from a paper read before the Royal Society, December 21, 1865.]

ON re-determining the co-efficients of expansion of water, they were found not to agree with Kopp's, and as his are results generally used by chemists, it may not be here out of place to give the new values.

It was found that the expansion of water between 4° and 100° may conveniently be expressed between 4° and 32° by the formula

$$V_t = 1 - 0.0000025300 (t - 4) + 0.0000083890 (t - 4)^2 - 0.00000007173 (t - 4)^3,$$

and between 32° and 100° by

$$V_t = 0.999695 + 0.0000054724t^2 - 0.000000011260t^3.$$

The values calculated from these formulæ for the volume occupied by water at different temperatures are given in Table I. from degree to degree, together with the differences for each degree.

TABLE I.

T°. C.	Volume of water at T°.	Difference per 1°.	T°. C.	Volume of water at T°.	Difference per 1°.	T°. C.	Volume of water at 1°.	Difference per 1°.
4	1.000000	0.000006	37	1.006616	0.000355	69	1.022050	0.000598
5	1.000006		38	1.006979	363	70	1.022648	
6	1.000028		39	1.007351	372	71	1.023252	
7	1.000066		40	1.007730	379	72	1.023861	
8	1.000119		41	1.008118	388	73	1.024477	
9	1.000188		42	1.008514	396	74	1.025099	
10	1.000271		43	1.008918	404	75	1.025727	
11	1.000369		44	1.009331	413	76	1.026361	
12	1.000479		45	1.009751	420	77	1.027000	
13	1.000604		46	1.010179	428	78	1.027646	
14	1.000742	138	47	1.010614	435	79	1.028296	650
15	1.000892	150	48	1.011059	445	80	1.028953	657
16	1.001054	162	49	1.011510	451	81	1.029615	662
17	1.001227	173	50	1.011969	459	82	1.030283	668
18	1.001412	185	51	1.012435	466	83	1.030956	673
19	1.001608	196	52	1.012909	474	84	1.031634	678
20	1.001814	206	53	1.013391	482	85	1.032318	684
21	1.002029	215	54	1.013879	488	86	1.033007	689
22	1.002254	225	55	1.014376	497	87	1.033701	694
23	1.002488	234	56	1.014879	503	88	1.034400	699
24	1.002731	243	57	1.015390	511	89	1.035104	704
25	1.002982	251	58	1.015907	517	90	1.035813	709
26	1.003241	259	59	1.016432	525	91	1.036527	714
27	1.003507	266	60	1.016964	532	92	1.037245	718
28	1.003780	273	61	1.017502	538	93	1.037969	724
29	1.004059	279	62	1.018047	545	94	1.038687	728
30	1.004345	286	63	1.018599	552	95	1.039429	732
31	1.004635	290	64	1.019158	559	96	1.040166	737
32	1.004931	296	65	1.019724	566	97	1.040907	741
33	1.005249	318	66	1.020296	572	98	1.041653	746
34	1.005578	329	67	1.020874	578	99	1.042404	751
35	1.005916	338	68	1.021459	585	100	1.043159	755
36	1.006261	345			591			

The values obtained by different observers for the volumes occupied by water at different temperatures, the volume at 4° being taken equal to 1, are given in Table II.

TABLE II.

T.	Kopp.*	Despretz.†	Pierre.‡	Hagen.§	Matthiessen.
4	1·000000	1·000000	1·000000	1·000000	1·000000
10	1·000247	1·000268	1·000271	1·000269	1·000271
15	1·000818	1·000875	1·000850	1·000849	1·000892
20	1·001690	1·001790	1·001717	1·001721	1·001814
30	1·004187	1·004330	1·004195	1·004250	1·004345
40	1·007654	1·007730	1·007636	1·007711	1·007730
50	1·011890	1·012050	1·011939	1·011994	1·011969
60	1·016715	1·016980	1·017243	1·017001	1·016964
70	1·022371	1·022550	1·023064	1·022675	1·022648
80	1·028707	1·028850	1·029486	1·028932	1·028953
90	1·035524	1·035660	1·036421	1·035715	1·035813
100	1·043114	1·043150	1·043777	1·042969	1·043159

It will be seen from the foregoing table that Kopp's values are lower than the others; and bearing in mind that the co-efficient of expansion of mercury, namely, 0·000178, when deduced by means of these, falls below that obtained by Regnault, namely, 0·0001815, but when deduced from my own, namely, 0·0001812, agrees closely with Regnault's, we are led to conclude that Kopp's values must be somewhat incorrect.

* Pogg. Ann. xcii. 42.

† Ann. Ch. Phys. lxx 1.

‡ Ann. Ch. Phys. [3] xiii 325. Calculated by Frankenheim, Pogg. Ann. xcvi. 451.

§ Abhandlungen d. k. Acad. der Wissensch. zu Berlin, 1865.

VI.—*Contributions to our Knowledge of the Chemical Action of Sunlight upon Sensitive Photographic Papers.*

By CHARLES R. WRIGHT, B.Sc. (Student in the Laboratory of Owens College, Manchester).

IN a paper published in the journal of the Chemical Society (Series II. vol. iii., p. 183) by Mr. A. McDougall, a method of measuring the relative sensitiveness to light of photographic papers is described, and the results detailed of a series of measurements, giving the relative sensitiveness of papers salted with solutions of different strengths of sodium-chloride, potassium-chloride, ammonium-chloride, and potassium-bromide, and afterwards floated upon a strong silver-nitrate bath of constant composition. From these experiments it appears that *the sensitiveness of a photographic paper depends solely on the quantity of the halogen contained in the salting solution, and that it is not influenced by the metal with which the halogen is combined*; for, if the results of his experiments on papers salted in solutions of chlorides of varying strengths be graphically represented with percentages of chlorine as ordinates, and relative sensitivenesses as abscissæ, the three curves obtained with solutions of sodium-, potassium-, and ammonium-chlorides will be found to coincide within the limits of experimental error. This conclusion is also borne out by the fact that papers prepared with solutions of potassium-, sodium-, ammonium-, and barium-chlorides, in such a manner that equal quantities of chlorine were contained in each, were all found to possess an equal degree of sensitiveness, whilst the same was also found to be true for the corresponding bromides.

It next becomes of interest to examine the relative sensitivenesses of papers salted with different halogens; to compare, for instance, the sensitiveness of a paper salted with a solution containing 1 per cent. of potassium-chloride with that of one salted with a solution containing an equivalent quantity of bromine, or with one in which half the chlorine is replaced by its equivalent of bromine or iodine. The following investigation was undertaken,

at Dr. Roscoe's suggestion, for the purpose of examining these questions.

The method described in the above-mentioned paper may be shortly explained thus: Let us suppose that papers A, B, C, &c., whose relative sensitiveness are to be determined, are exposed in the disc-photometer for known relative times t_1, t_2, t_3 , &c., the points identical in shade with A, B, C, &c., after exposure, being read off on a pendulum-strip of standard paper (or on a fixed calibrated strip); let the readings be a, b, c , &c. be millimetres, and let the times corresponding to these readings (that is, the relative times that standard paper would take to assume the tints gained by the papers A, B, C, &c.) be called T_1, T_2, T_3 , &c. Hence the ratio of the time taken by paper A to assume its particular tint to that required by standard paper to assume the same tint is $t_1 : T_1$ or $1 : \frac{T_1}{t_1}$; and similarly, the ratio of the time taken by paper B to assume its peculiar tint to that required by standard paper to assume this same tint, is $1 : \frac{T_2}{t_2}$; and so on for the others—that is, the sensitiveness of A compared with standard paper is $\frac{T_1}{t_1}$, and that of B compared with standard paper is $\frac{T_2}{t_2}$; hence, if the sensitiveness of A be taken as unity, that of B is $\frac{T_2 t_1}{t_2 T_1}$; similarly the sensitiveness of C and the others with respect to A are obtained.

It hence follows, that when pieces of the same paper are exposed at once in the disc-photometer for the times respectively t_1, t_2, t_3, \dots and read off as before, the fractions $\frac{T_1}{t_1}, \frac{T_2}{t_2}, \frac{T_3}{t_3}, \dots$ must be equal, as each fraction represents the sensitiveness of the paper experimented on with respect to standard paper. It was, however, found, on exposing papers prepared with different halogens in the photometer, that the values thus obtained were by no means constant when the value of the t 's varied, whilst if the values of the t 's remained the same, constant values were obtained. Thus, for instance, when chlor-iodide and chloro-brom-iodide papers were exposed together, the ratio of the t 's being 1.00 to 0.40; the following agreeing values were obtained for the sensitiveness of the latter paper as compared with that of the former.

Exp. 1.—2·16	Exp. 5.—2·32	Exp. 9.—2·46
„ 2.—2·17	„ 6.—2·36	„ 10.—2·53
„ 3.—2·29	„ 7.—2·38	„ 11.—2·62
„ 4.—2·31	„ 8.—2·40	
Mean 2·36.		

When, however, the ratio of the t 's was 1·00 to 0·63, the mean of five similarly agreeing determinations gave the value 1·65. It hence follows that for one or other of these two papers (or, perhaps, for both) the values of the fractions $\frac{T_1}{t_1}$, $\frac{T_2}{t_2}$, $\frac{T_3}{t_3}$. . . are not constant, which may be expressed by saying that the value of $\frac{T_n}{t_n}$ is, for this paper, not constant.

Similarly on comparing bromide and brom-iodide papers, the mean of twenty experiments gave the following numbers:—

Ratio of the t 's.	Ratio of sensitiveness of brom-iodide paper to that of bromide.
1·00 to 2·552	0·297 to 1·00
„ 1·867	0·393 „
„ 1·678	0·411 „
„ 0·720	0·706 „
„ 0·704	0·792 „

Before pursuing this point any further, it became necessary to ascertain (1) that the disc-photometer fulfils its functions, and (2) that the phenomena of photochemical induction do not interfere with the accuracy of the results.

(1.) In order to test the correct working of the photometer, papers salted with potassium-chlor-iodide, chloro-brom-iodide, and chloro-bromide, respectively, were insolated (*a*) in the disc photometer, and (*b*) by direct exposure, for, as nearly as possible, the same relative times in both cases. The following numbers were obtained as the relative sensitiveness of these three papers as the mean of twelve experiments:—

Disc photometer.	Direct exposure.
Chlor-iodide 1·00	1·00
Chloro-brom-iodide 2·30	2·32
Chloro-bromide .. 3·09	2·99

Also papers soaked in solutions of sodium-chloride, containing respectively 0·5, 1·0, 2·0, and 4·0 per cent. of that salt, were similarly insolated, giving the following numbers as the mean of eleven experiments :—

Disc photometer.		Direct exposure.
0·5 per cent.	0·781	0·821
1·0 „	1·000	1·000
2·0 „	1·787	1·788
4·0 „	3·018	2·986

Further, normal paper (that soaked in a 3 per cent. sodium-chloride solution) was insolated in the photometer, and the values of the fractions $\frac{T_1}{t_1}$, $\frac{T_2}{t_2}$, &c., were found to be sensibly uniform whether the insolation were performed in bright sunlight or diffused daylight; precisely similar results were obtained with 4 per cent. potassium-chloride paper.

(2.) For the purpose of testing the influence of photochemical induction, papers salted in potassium-chloride, bromide, and brom-iodide solutions were severally exposed to the action of direct sunlight for a known time; and, at the same time, portions of the same papers were exposed under a small disc (of which one-sixth of the area was cut away in the form of sectors) for six times that interval, so that in the two cases the absolute time of exposure was identical, but in the latter case the exposure was interrupted by a succession of dark phases; hence the effect of photochemical induction, if appreciable, would be rendered manifest by the greater darkening of the paper in the second case. On reading off the various insolated papers on a pendulum-strip, the following ratios were obtained for the tints assumed .—

Chloride paper.	Mean of 8 experiments.
By direct exposure.	0·991
By disc photometer	1·000

Bromide paper.	Mean of 8 experiments.
By direct exposure.	0·989
By disc photometer	1·000

Brom-iodide paper.	Mean of 6 experiments.
By direct exposure.	0·917
By disc photometer	1·000

The differences here observed are not greater in amount than can easily be accounted for by the action of the stray daylight which must inevitably get under the small revolving disc; in confirmation of this, it was observed that brom-iodide paper, with which the greatest difference was thus obtained, was considerably blackened by exposure to light of so feeble an intensity as to have no appreciable action on either the corresponding chloride or bromide paper.

It is hence manifest that the differences in the relative sensitiveness of papers observed above, are neither due to photochemical induction, nor to any abnormal action in the disc-photometer, and it therefore appears that they must have been caused by the differences in the ratios of the t 's; and hence we must conclude that *papers prepared with different halogens do not all darken at the same relative rates*. This conclusion may be expressed as follows:—If standard paper be exposed to a constant source of light, it assumes a definite series of tints in the relative times 1, 2, 3, 4 . . . ; if, however, bromide paper be exposed to this same source of light, the relative times in which it assumes the same series of tints are not 1, 2, 3, 4 . . . , but are in some other proportion; and the same is (probably) true for all papers prepared with other halogens.

Before proceeding to determine what this proportion is for each paper, it becomes necessary to examine whether this proportion is the same for a paper salted with a strong solution of any halogen as for one salted with a weak solution of the same halogen. For this purpose, papers salted in a 10 per cent. sodium-chloride solution were exposed in the disc-photometer and read off on a calibrated strip: hence the ratios of the t 's are known from the positions of the papers in the photometer, whilst the ratios of the T 's are obtained from the calibration table of the strip. The following numbers were obtained as the mean of four agreeing determinations:—

(The column headed t represents the t 's all reduced to the greatest of them as unity; that headed T denotes the T 's all similarly reduced; the column headed R represents the ratios of the numbers in the t column to the corresponding ones in the T column; while that headed Diff. denotes the + or - differences of these ratios from their mean.)

<i>t.</i>	T.	R.	Diff.
1·000	1·000	1·000	— 0·06
·742	·781	1·05	— 0·01
·590	·588	1·00	— 0·06
·490	·534	1·08	+ 0·02
·420	·477	1·13	+ 0·07
·392	·427	1·09	+ 0·03

In a precisely similar manner the following numbers were obtained with 0·5 per cent. sodium-chloride paper as the mean of four agreeing experiments :—

<i>t.</i>	T.	R.	Diff.
1·000	1·000	1·00	— 0·04
·742	·787	1·06	+ 0·02
·590	·611	1·03	— 0·01
·490	·527	1·07	+ 0·03
·420	·445	1·06	+ 0·02
·392	·409	1·05	+ 0·01

Hence it appears that with these chloride solutions, which present great differences in their strengths, the numbers in the *t* column do not differ appreciably from the corresponding ones in the T column : hence it follows that *the relative rates of darkening of the 10 per cent., 3 per cent., and 0·5 per cent. sodium-chloride papers are, within the limits of experimental error, identical.* If

$\left(\frac{T_n}{t_n}\right)$ denote the values of the ratios of the numbers in the *t* column to the corresponding ones in the T column, this may be expressed by saying that the value of the fraction $\left(\frac{T_n}{t_n}\right)$ (which

Mr. McDougall's experiments have shown not to be a function of the metal with which the halogen of the salting solution is combined) *is a function of neither the strength of the salting solution nor of the time of exposure*, in the case of chloride papers.

A similar set of experiments performed with bromide solutions yielded the following numbers as the mean of nine experiments :—

(A) 6·386 per cent. potassium-bromide paper.

<i>t.</i>	T.	R.	Diff.
1·000	1·000	1·00	— 0·51
·742	·920	1·24	— 0·27
·590	·858	1·45	— 0·06
·490	·838	1·71	+ 0·20
·420	·773	1·84	+ 0·33
·392	·721	1·84	+ 0·33

(B) 0·25 per cent. potassium-bromide paper.

<i>t.</i>	T.	R.	Diff.
1·000	1·000	1·00	— 0·56
·742	·935	1·25	— 0·31
·590	·871	1·47	— 0·09
·490	·843	1·72	+ 0·16
·420	·813	1·93	+ 0·37
·392	·782	2·00	+ 0·44

From these numbers, it appears that with bromide papers the value of the fraction $\left(\frac{T_n}{t_n} \right)$, (1) *is a function of the time of exposure*, and (2) *is not a function of the strength of the salting solution*,—since the numbers in the column of ratios are, within experimental error limits, identical both with the strong and with the weak solutions. It is, therefore, clear that if the relative sensitivenesses of papers are to be compared, some particular tint must be taken as a standard of reference. If we know the relation between the relative times taken by papers prepared with chlorine as halogen, and those by the papers experimented on, to gain a certain definite series of tints, and also the relative sensitivenesses of these papers with respect to any one of these tints, we can then calculate their relative sensitivenesses with respect to any other of these tints.

In order to determine the relative times taken by papers prepared with various halogens to gain the same definite series of tints, papers salted in the undermentioned solutions were insolated in the disc-photometer and read off on a carefully calibrated strip:—

Potassium Bromide	containing 6·386 per cent. of KBr.
„ Brom-iodide	„ 4·452 per cent. of KI, and 3·193 of KBr.
„ Chloro-bromide	„ 2·000 per cent. of KCl,

Potassium-Chlor-iodide containing 2·000 per cent. of KCl,
and 4·452 of KI.
2·128 of KBr.
and 2·969 of KI.

„ *Chloro-brom-iodide* „ 1·333 per cent. of KCl,

All the above solutions contain precisely as much potassium as exists in a solution containing 4 per cent. of potassium-chloride. The mixed solutions (brom-iodide, &c.) contain equal quantities of potassium combined with different halogens. In order to verify, beyond doubt, the results thus obtained, the same papers were exposed in the pendulum photometer and read off as before; whilst, as a third check, the same papers were directly exposed to sunlight for known times and read off. In order to estimate the amount of accuracy attainable by these latter methods, 4 per cent. potassium-chloride papers were thus insolated and read off, giving the following numbers:—

(The same symbols, *t*, T, R, and Diff., are used as the headings of the columns, and with the same meanings as in the previous experiments.)

(A) Insolated in the pendulum photometer; mean of three agreeing experiments.

<i>t</i> .	T.	R.	Diff.
1·000	1·000	1·000	— 0·002
·876	·871	·995	— 0·007
·765	·764	·999	— 0·003
·655	·657	1·003	+ 0·001
·541	·548	1·012	+ 0·010
·414	·416	1·005	+ 0·003

(B) Insolated by direct exposure; mean of four agreeing experiments.

<i>t</i> .	T.	R.	Diff.
1·000	1·000	1·000	— 0·004
·857	·842	·982	— 0·022
·800	·810	1·012	+ 0·008
·750	·742	·989	— 0·015
·714	·757	1·060	+ 0·056
·600	·606	1·009	+ 0·005
·571	·584	1·023	+ 0·019
·500	·501	1·002	— 0·002
·429	·435	1·014	+ 0·010
·400	·380	·950	— 0·054

The smallness of the differences thus obtained shows that fair results may be anticipated by each method.

The following are the numbers obtained with bromide paper :—

1. By the disc-photometer (mean of five experiments).
2. By the pendulum-photometer (mean of four experiments).
3. By direct exposure (mean of eight experiments).

(1) By the disc-photometer :—

<i>t.</i>	T.	R.
1·000	1·000	1·000
·742	·920	1·240
·590	·858	1·455
·490	·838	1·711
·420	·773	1·840
·392	·721	1·839

(2) By the pendulum-photometer :—

<i>t.</i>	T.	R.
1·000	1·000	1·000
·876	·961	1·097
·765	·921	1·204
·655	·890	1·359
·541	·839	1·551
·414	·786	1·904

(3) By direct exposure :—

<i>t.</i>	T.	R.
1·000	1·000	1·000
·750	·907	1·208
·667	·828	1·242
·600	·894	1·489
·500	·713	1·425
·400	·740	1·850
·333	·677	2·031
·250	·486	1·943
·200	·541	2·704

The following values are obtained for the *mean bromide curve* by graphical interpolation, the numbers in the column *t* being represented as abscissæ, and those in the column T as ordinates :—

MEAN BROMIDE CURVE.

<i>t.</i>	T.	R.
1·000	1·000	1·000
·950	·988	1·040
·900	·975	1·084
·850	·960	1·129
·800	·945	1·181
·750	·930	1·240
·700	·910	1·300
·650	·890	1·369
·600	·860	1·433
·550	·830	1·509
·500	·790	1·580
·450	·740	1·644
·400	·685	1·713
·350	·625	1·786
·300	·565	1·887
·250	·500	2·000
·200	·430	2·150

These numbers signify that if two pieces of any paper prepared with *chlorine* as halogen gain certain tints on exposure to sunlight for the relative times 1·000 and 0·790, two pieces of any paper prepared with *bromine* as halogen would gain the same tints on exposure to the same light in the relative times 1·000 and 0·500; and so on.

The following table gives the values for the *mean brom-iodide curve*, obtained in a precisely similar way from four experiments with the disc-photometer, four with the pendulum photometer, and four by direct exposure :—

MEAN BROM-IODIDE CURVE.

<i>t.</i>	T.	R.
1·000	1·000	1·000
·900	·980	1·089
·800	·960	1·200
·700	·930	1·367
·600	·900	1·500
·500	·850	1·700
·400	·780	1·950
·300	·700	2·333
·200	·600	3·000

It appears from these numbers that, if the sensitivenesses of a chloride and a brom-iodide paper be compared, the number expressing the sensitiveness of the latter with respect to the former will be three times as great with respect to a tint gained by the chloride paper in a time 0·6, as that with respect to a tint gained by the chloride paper in a time 1·0 : for that obtained in the first instance will be $\frac{0\cdot600}{0\cdot200} \times x$ (where x denotes the absolute ratio of the t to the T) ; and that in the second instance $\frac{1\cdot000}{1\cdot000} \times x$.

The mean of four experiments with the disc-photometer gave the following numbers for chloro-bromide paper.

MEAN CHLORO-BROMIDE CURVE.

t .	T .	R .
1·000	1·000	1·000
·900	·970	1·078
·800	·930	1·162
·700	·880	1·257
·600	·820	1·367
·500	·730	1·460
·400	·610	1·525
·300	·480	1·600

The mean of four experiments with the disc photometer gave the following numbers for chlor-iodide paper :—

MEAN CHLOR-IODIDE CURVE.

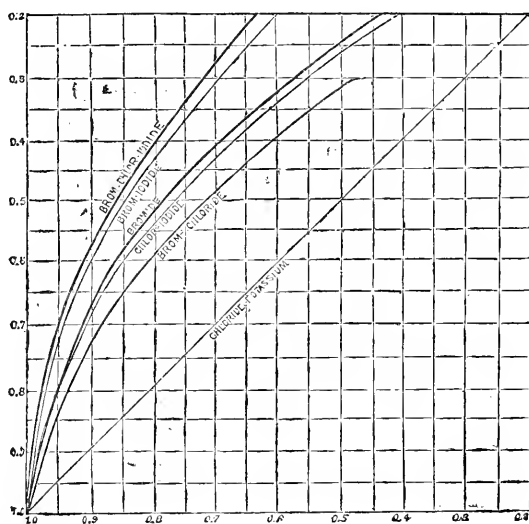
t .	T .	R .
1·000	1·000	1·000
·900	·980	1·089
·800	·950	1·178
·700	·910	1·300
·600	·850	1·417
·500	·770	1·540
·400	·675	1·688
·300	·560	1·867
·200	·420	2·100

The mean of four experiments with the disc-photometer gave the following numbers for chloro-brom-iodide paper :—

MEAN CHLOR-BROM-IODIDE CURVE.

<i>t.</i>	<i>T.</i>	<i>R.</i>
1·000	1·000	1·000
·900	·980	1·089
·800	·960	1·200
·700	·930	1·329
·600	·900	1·500
·500	·860	1·720
·400	·800	2·000
·300	·730	2·433
·200	·640	3·200

The annexed illustration shows the curves thus obtained for these five papers, the corresponding chloride line being represented by the straight diagonal line :—



The values of these five curves may be all represented at once by the following table, which gives the relative times that any of the above papers take to assume (when exposed to a constant source of light) the series of tints assumed by chloride paper in the times 1·000, 0·975, 0·950, &c. :—

Chloride.	Bromide.	Brom-iodide.	Chloro-bromide.	Chlor-iodide.	Chloro-brom-iodide.
1·000	1·000	1·000	1·000	1·000	1·000
·975	·875	·810	·910	·875	·790
·950	·800	·735	·840	·800	·700
·925	·730	·660	·780	·735	·620
·900	·670	·580	·730	·680	·560
·850	·585	·500	·650	·600	·470
·800	·515	·420	·580	·535	·390
·750	·455	·350	·525	·480	·320
·700	·410	·290	·475	·425	·265
·650	·360	·240	·430	·375	·220
·600	·320	·200	·390	·335	
·550	·280		·355	·295	
·500	·240		·320	·260	
·450	·200		·290	·230	
·400				·200	

These curves were obtained by the use of salting-solutions equivalent to a 4 per cent. potassium-chloride solution; but it having been previously shown that the rates of darkening of all chloride and bromide papers are respectively identical, whatever be the strengths of the salting solutions, this may be assumed to be true for all the others: hence *the above numbers represent the relative rates of darkening of any papers prepared with these five halogens.*

If the numbers for chloride paper be represented generally by T_c , and those for bromide papers by T_b , the connection between T_c and T_b is approximately given by the formula—

$$T_c = 2\cdot4 - T_b 1\cdot9(T_b)^2 + 0\cdot5(T_b)^3.$$

By the aid of this table, the relative sensitivenesses of any of the above papers with respect to any given tint can be calculated, when their relative sensitivenesses with respect to any other are known. For example, let it be required to compare the relative sensitivenesses of 4 per cent. chloride and the equivalent chlor-iodide, chloro-bromide, bromide, and brom-iodide papers, with respect to the tint taken as the normal in photometric observations (viz., that gained by 3 per cent. sodium-chloride paper on exposure for one second to light of the unit of intensity). As the mean of five experiments, it was found that on exposure for the relative times 1·000, 0·742, and 0·562, chloride, chlor-iodide, and bromide papers assumed

tints which standard paper would have assumed (on exposure to light of the unit of intensity) in the times 0.509, 0.682, and 0.905 seconds. Let x , y , and z respectively represent the relative times in which the three papers would assume the normal tint, then their relative sensitiveness with respect to this tint are respectively $\frac{1}{x}$, $\frac{1}{y}$, and $\frac{1}{z}$; or 1.000, $\frac{2}{y}$, and $\frac{2}{z}$. Thus—

$$(1.) \quad x : 1.000 : : 1.000 : 0.509,$$

$$\text{or } x = \frac{1.000}{0.509} = 1.965.$$

(2.) From the table, the relative times in which chlor-iodide paper would gain tints assumed by chloride papers in the relative times 1.000 and 0.682, are 1.000 and 0.407.

$$\text{Hence } y : 0.742 : : 1.000 : 0.407,$$

$$\text{or } y = \frac{0.742}{0.407} = 1.822.$$

(3.) From the table, the relative times in which bromide paper would gain tints assumed by chloride paper in the relative times 1.000 and 0.906, are 1.000 and 0.685.

$$\text{Hence } z : 0.562 : : 1.000 : 0.685,$$

$$\text{or } z = \frac{0.562}{0.685} = 0.820.$$

$$\text{Hence } \frac{x}{y} \text{ and } \frac{x}{z} \text{ are respectively } \frac{1.965}{1.822} \text{ and } \frac{1.965}{0.820},$$

$$\text{or } 1.078 \text{ and } 2.396.$$

That is, the relative sensitivenesses of 4 per cent. chloride paper and its equivalent chlor-iodide and bromide papers with respect to the normal tint, are 1.000, 1.078, and 2.396 respectively.

Again, as the mean of 12 experiments, it was found that chlor-iodide and chloro-bromide papers, on exposure for the relative times 1.000 and 0.431, gain tints which normal paper would (on exposure to light of the unit of intensity) gain in the times 0.483 and 0.628 seconds.

Calculating as before, the relative sensitivenesses of these two papers are found to be $\frac{1}{4.000}$ and $\frac{1}{1.072}$, or 1.078 and 4.022.

Again, the mean of 10 experiments gave the following numbers for bromide and brom-iodide papers :—

	Bromide.	Brom-iodide.	Bromide.	Brom-iodide.	Bromide.	Brom-iodide.
Relative times of exposure	1·000	1·867	1·000	1·678	1·000	2·552
Times in which standard paper would assume the tints gained by the papers exposed.....	0·861	0·621	0·943	0·648	0·732	0·553
Relative sensitivenesses ..	2·396	4·624	2·396	4·002	2·396	2·612
Mean relative sensitivenesses			Bromide.	Brom-iodide.		
			2·396	4·060		

Hence the relative sensitivenesses of the above 5 papers with respect to the normal tint are—

<i>Chloride</i>	1·000
<i>Chlor-iodide</i>	1·078
<i>Chloro-bromide</i>	4·022
<i>Bromide</i>	2·396
<i>Brom-iodide</i>	4·060

In a similar way their relative sensitivenesses with respect to any other tint may be calculated.

It having been observed, during these experiments, that the same result was obtained whether the papers were exposed to the full noonday sun, to the evening sun, or in the shade, it became interesting to observe what effects were produced upon each paper by variations in the intensity of the light acting upon them, the time of exposure being constant. In order to observe this—

(1.) A brass plate perforated with small circular holes, the diameters of which were accurately measured by a micrometer, was fitted light-tight into the wall of a dark room, so that the sun could shine perpendicularly upon the plate. A sheet of prepared paper to receive the images of the sun formed by the small holes was placed at such a distance from the plate, that the angle subtended by the largest hole from the paper was less than the apparent diameter of the sun; all the images were thus kept of the same size: hence the intensity of light under each image was proportional to the square of the diameter of the hole forming that image. (2.) The prepared papers were exposed at the bottom of vertical cylinders, coated internally with black paper, and covered over with metal caps having round holes of varying sizes drilled in them; these holes varied in diameter between 77·5 and 25 millimetres, the cylinders being 5 decimetres high and 1 deci-

metre in diameter. By this means, only diffused light from the zenith was employed, the intensities of the light being, as before, proportional to the squares of the diameters of the holes. As a check on the accuracy of the results obtainable by these two methods, 4 per cent. potassium-chloride paper was thus exposed with the following results. (The column A represents the relative intensities of the acting light; the column T the relative times in which standard paper, on exposure to a constant source of light, would gain the tints assumed by the papers experimented on, the largest being taken as unity; the column R gives the ratios of the numbers in the A column to the corresponding ones in the T column; and the column Diff. gives the differences of the numbers in the R column from their mean. In accordance with the law of Professors Bunsen and Roscoe, the numbers in the column R should be sensibly constant, provided that no serious imperfection exists in the working of the apparatus employed.)

4 per cent. potassium-chloride paper exposed under the perforated plate :—

MEAN OF TWO EXPERIMENTS.

A.	T.	R.	Diff.
1·000	1·000	1·00	— 0·07
·701	·777	1·11	+ 0·04
·663	·757	1·14	+ 0·07
·653	·719	1·10	+ 0·03
·520	·496	·96	— 0·11
·394	·399	1·01	— 0·04
·299	·344	1·15	+ 0·08

4 per cent. potassium-chloride paper exposed in the cylinders :—

MEAN OF FOUR EXPERIMENTS.

A.	T.	R.	Diff.
1·000	1·000	1·00	— 0·01
·719	·734	1·02	+ 0·01
·595	·625	1·05	+ 0·04
·444	·418	·94	— 0·07
·428	·443	1·03	+ 0·02
·326	·330	1·01	+ 0·00

The numbers in the columns of differences being in no case large, tolerably accurate results may be anticipated by either method.

On exposing bromide paper (equivalent to 4 per cent. potassium-chloride), the following results were obtained as the mean of five experiments with the perforated plate, and of three with the cylinders.

Experiments with the cylinders and bromide paper :—

A.	T.	R.
1·000	1·000	1·000
·595	·881	1·479
·326	·521	1·601
·145	·331	2·289

Experiments with the perforated plate and bromide paper :—

A.	T.	R.
1·000	1·000	1·000
·945	·993	1·051
·932	·992	1·065
·759	·928	1·223
·741	·918	1·238
·701	·916	1·307
·663	·912	1·377
·653	·904	1·384
·575	·842	1·464
·562	·859	1·527
·520	·809	1·557
·426	·749	1·759
·394	·691	1·752
·299	·569	1·902
·258	·590	2·286
·191	·390	2·041
·134	·377	2·814

On graphical representation, the numbers in the columns A being represented as abscissæ, and those in the columns T as ordinates, these results are found to coincide, giving *a mean curve identical with that derived from the experiments with the disc-photometer* (p. 42) ; in other words, bromide papers on exposure to a constant source of light for times $t_1, t_2, t_3 \dots$, gain certain tints ; and on exposure for the same time to lights of intensities $A_1 A_2 A_3 \dots$ the same tints are gained : then

$$t_1 A_1 = t_2 A_2 = t_3 A_3 = \dots = \text{constant.}$$

That is, *the law enunciated by Profs. Bunsen and Roscoe for*

standard chloride paper is also true for bromide papers; viz., that the same tint is gained by exposing the papers for a time 1 to an intensity 10, as is gained on exposure for a time 10 to an intensity 1, or for a time 2 to an intensity 5; and so on.

Hence, if a pendulum strip be made with bromide paper, and the same paper be exposed to varying intensities of light, and the tints thus produced be read off on the bromide pendulum strip, it should be found that the numbers from the strip calibration-table are to one another in the same proportion as the numbers indicating the intensities of light. On trying the experiment, however, it was found impossible to read off on the bromide strip, owing to the slight difference in tint between the two ends.

On exposure of brom-iodide paper in the same ways, the following numbers were obtained as the mean of six experiments by the aid of the perforated plate (direct sunlight), and of four by means of the cylinders (diffused light).

Brom-iodide paper, with direct sunlight:—

A.	T.	R.
1·000	1·000	1·000
·786	·914	1·163
·551	·843	1·530
·521	·824	1·581
·513	·823	1·604
·409	·737	1·805
·310	·741	2·390
·235	·640	2·707
·106	·468	4·437
·060	·349	5·825

Brom-iodide paper with diffused daylight:—

A.	T.	R.
1·000	1·000	1·000
·719	·894	1·244
·428	·765	1·787
·234	·644	2·751
·104	·406	3·899

As with the bromide paper, these numbers are found, on graphical representation, to yield *a mean curve identical with that derived from the previous experiments with the disc-photometer, &c., (that is Bunsen and Roscoe's law is likewise true for this paper).*

On endeavouring to read off brom-iodide papers exposed to varying intensities of light on a brom-iodide pendulum strip, it was found impossible to get any trustworthy results, owing to the slight difference in tint between the two ends of the strip.

The following numbers were derived from the mean of four experiments with chloro-bromide paper with diffused light from the zenith (cylinders) :—

A.	T.	R.
1·000	1·000	1·000
·719	·837	1·164
·596	·844	1·416
·428	·601	1·404
·326	·471	1·414
·145	·357	2·460

These numbers, also, on graphical representation, give a *curve identical with that derived from the disc-photometer experiments.*

On reading off papers exposed to varying intensities of light (in the cylinders) on a chloro-bromide pendulum strip, the following numbers were obtained as the mean of four experiments. (The numbers in the column P are the relative times in which chloro-bromide paper would, on exposure to light of uniform intensity, gain the tints assumed by the papers experimented on: the columns A, R and Diff. have the same meanings as hitherto.)

A.	P.	R.	Diff.
1·000	1·000	1·00	— 0·08
·719	·702	·98	— 0·10
·595	·658	1·10	+ 0·02
·428	·450	1·05	— 0·03
·326	·410	1·26	+ 0·18

Considering the great difficulty of reading off correctly on a chloro-bromide pendulum strip, which exhibits much less gradation of tint than a chloride one, the differences are sufficiently small to show that *Bunsen and Roscoe's law is obeyed by this paper.*

On exposing chloriodide papers to diffused light of varying intensities (cylinders), the following numbers were obtained as the mean of four experiments :—

A.	T.	R.
1·000	1·000	1·000
·718	·924	1·286
·428	·719	1·680
·234	·463	1·979
·104	·314	3·019

These numbers also, on graphical representation, are found to yield *a mean curve identical with that derived from the disc-photometer experiments.*

Chlor-iodide papers exposed to varying intensities of light (cylinders), and read off on a chlor-iodide pendulum strip, yielded the following numbers as the mean of three experiments. (The column Q indicates the relative times in which chlor-iodide papers would assume the tints gained by those experimented on, on exposure to a constant source of light.)

A.	Q.	R.	Diff.
1·000	1·000	1·00	— 0·00
·719	·636	·88	— 0·12
·595	·579	·97	— 0·03
·428	·425	·99	— 0·01
·326	·382	1·17	+ 0·17

As the chloriodide pendulum strip shows much less gradation in tint than the chloride strip, these numbers show that *Bunsen and Roscoe's law is obeyed by this paper.*

By exposing chloro-brom-iodide paper to diffused light of varying intensities, the following numbers were obtained as the mean of four experiments :—

A.	T.	R.
1·000	1·000	1·000
·718	·921	1·280
·428	·837	1·955
·234	·716	3·061
·104	·494	4·749

On graphical representation, these numbers are found to give a *mean curve identical with that derived from the disc-photometer experiments.* On endeavouring to read off chloro-brom-iodide papers exposed to varying intensities of light, on a chloro-brom-iodide pendulum strip, no good results were obtainable, from the slight differences in tint between the two ends of the strip.

Since all the above papers obey Bunsen and Roscoe's law, the table given on p. 45 also denotes *the relative intensities of light to which pieces of any papers prepared with the above halogens must be exposed for the same time, in order to gain the same series of tints.*

The results obtained by the foregoing experiments, together with those previously obtained by Mr. McDougall, may be briefly summed up thus :—

(1.) Papers prepared with solutions of different alkaline chlorides darken to the same extents in the same *relative* times, no matter with what alkaline metal the chlorine be combined, and no matter what be the constant percentage of chlorine in the salting solution.

(2.) The same holds true for papers prepared with bromide solutions (and hence, probably, for all the others).

(3.) Photo-chemical induction does not exist to any appreciable extent with chloride, bromide, and brom-iodide papers (and hence, probably, with none of the others).

(4.) The relative times for which pieces of any one of the above papers must be exposed to light of a constant intensity in order to gain a definite series of tints vary with each paper.

(5.) The relative intensities of light to which pieces of any one of the above papers must be exposed for a constant time, in order to gain a definite series of tints, vary with each paper.

(6.) The relative times for which pieces of any one of the above papers must be exposed to light of a constant intensity in order to gain a definite series of tints, are in the same ratio to one another as are the relative intensities of light to which the same pieces must be exposed for a constant time in order to gain the same series of tints.

(7.) The relative times for which pieces of any one of the above papers must be exposed to a constant source of light in order to gain a given series of tints, or the relative intensities of light to which they must be exposed for a constant time to gain the same series of tints, are given by the table on p. 45.

(8.) By the aid of this table, the relative sensitivenesses of any of the above papers with respect to any particular tint can be calculated, when their relative sensitivenesses with respect to some one given tint are known.

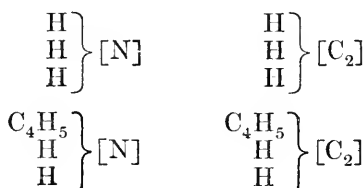
In conclusion, I beg to tender sincere thanks to Professor Roscoe for the valuable advice and assistance which he has given me in carrying out the above investigation.

VII.—*Prognosis of new Alcohols and Aldehydes.*

By Professor H. KOLBE, in Leipzig.

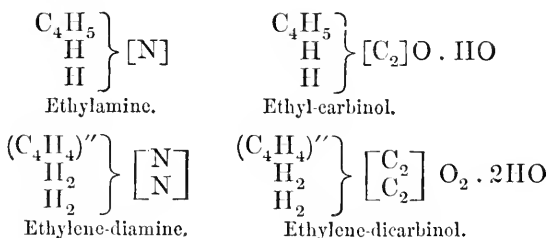
IN my several publications on Organic Chemistry, I have repeatedly directed attention to the probable existence of a class of compounds, related to the ordinary alcohols and aldehydes in the same manner as diamines and triamines are related to monamines.

In a former memoir on the Secondary Alcohols,* I placed ammonia and carbin,† ethylamine and ethylcarbin, in parallels, thus:—



and endeavoured to demonstrate, from the known existence of secondary and tertiary ammonias, the possibility of the existence of secondary and tertiary alcohols, several of which are now actually known.

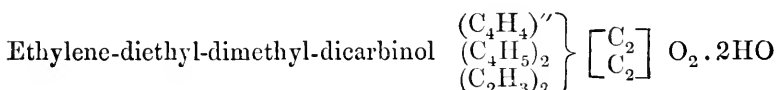
A similar parallel, drawn in a different direction, opens out a new field of chemical research. For just as diamines are produced by the substitution of diatomic radicals for hydrogen in ammonia, so may it be regarded as probable, or, I should rather say, predicted with certainty, that dicarbinols will be produced under similar circumstances from carbinols, as indicated by the following constitutional formulæ:—



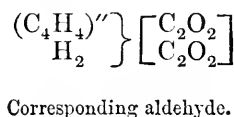
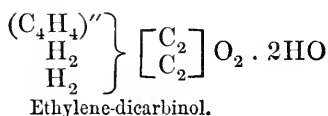
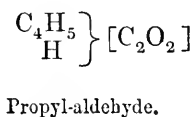
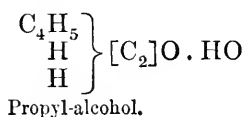
* Ann. Ch. Pharm. cxxxii, 102.

† For reasons developed in the memoir above referred to, I have proposed to designate *methyl* as “carbin,” *methylic alcohol* as “carbinol,” *ethylic alcohol* as “methyl-carbinol,” which names are used in the present communication.

Further, the replacement of the two pairs of typic hydrogen-atoms in ethylene-dicarbinol by diatomic or monatomic radicals, will give rise to the formation of secondary and tertiary dicarbinols, *e.g.* :—

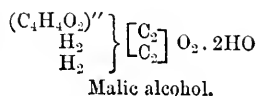
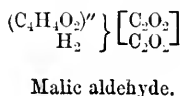
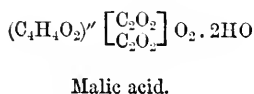
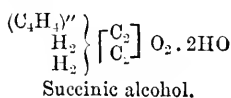
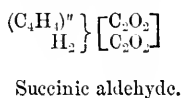
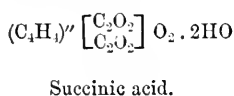


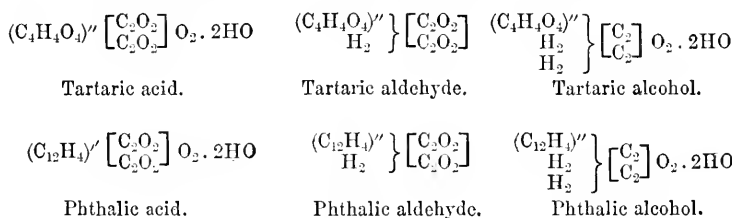
Ordinary alcohols are converted into aldehydes by substitution of oxygen for one of their typical hydrogen-atoms ; and in like manner, ethylene-dicarbinol may be expected to yield an aldehyde by oxidation and elimination of a pair of its typical hydrogen-atoms ; thus :—



The acid corresponding to ethylene-dicarbinol and its aldehyde, and resulting from the latter by oxidation of the last pair of hydrogen-atoms, is succinic acid $(\text{C}_4\text{H}_4)'' \left[\begin{array}{c} \text{C}_2\text{O}_2 \\ \text{C}_2\text{O}_2 \end{array} \right] \text{O}_2 \cdot 2\text{HO}$.

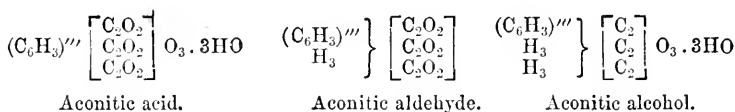
These considerations lead to the further conclusion that other dibasic acids, as well as succinic acid, will have their corresponding aldehydes and alcohols. Those of malic, tartaric, and phthalic acid will be symbolically represented as follows :—





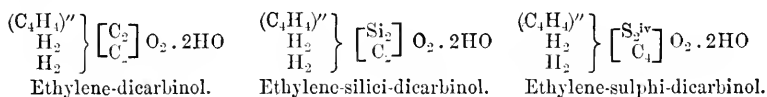
Malic alcohol is merely isomeric, not identical with diethylenic alcohol.

Evidently, also, there must exist tricarbinols, with their aldehydes, corresponding to the tribasic acids. The composition of the aldehyde and alcohol of aconitic acid are represented by the formulæ—

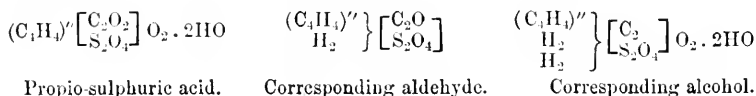


It may be predicted that the aldehydes, and probably also the alcohols, of the tribasic acids, will exhibit acid properties.

Hofmann has shown that one of the two nitrogen-atoms in a diamine may be replaced by phosphorus; and in like manner, it is highly probable that in the dicarbinols a double atom of carbon may be replaced by another tetra-equivalent element, for example, by silicium (Si_2), perhaps also by the tetratomic sulphur of sulphurous acid, whereby new alcohols with mixed radicals will be produced; thus—



Lastly, if succinic acid has an aldehyde and an alcohol belonging to it, we may expect also that the analogously constituted propio-sulphuric acid, and similar polybasic acids with mixed radicals, will have their corresponding aldehydes and alcohols, as represented by the following constitutional formulæ :—



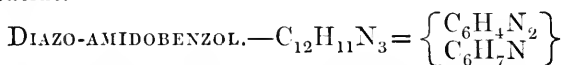
I am at present engaged in endeavouring to obtain the alcohols and aldehydes of polybasic acids from the acids themselves, and hope soon to be able to communicate positive results.

VIII.—*On a new Class of Organic Compounds in which Hydrogen is replaced by Nitrogen.*

By PETER GRIESS.

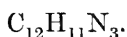
III.

THE researches published in my two preceding papers on the substitution of nitrogen for hydrogen in organic compounds were confined exclusively to bodies belonging to the acid type. The idea naturally presented itself of also submitting organic bases to the action of nitrous acid. I have chosen for this purpose those which are closely related to the amido-acids of the aromatic series. I have thus obtained new nitrogen-compounds presenting, in their composition and deportment, a well characterised series parallel to the diazoacids.

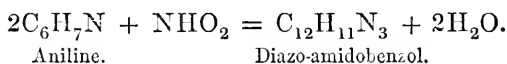


In order to prepare this body, aniline [(amidobenzol = $\text{C}_{12}\text{H}_5(\text{NH}_2)$] is dissolved in from six to ten times its volume of ordinary spirit; and a slow stream of nitrous acid is passed into this solution, which must always be kept cool, until the whole of the aniline has disappeared. This point is reached as soon as the oily residue, obtained by evaporating a small quantity of the solution on a watch-glass, solidifies to a semi-crystalline mass. The solidification however occasionally, and especially in the summer, takes place after some time only. In that case the completion of the process is easily recognised by testing whether the oily residue remains insoluble in dilute acetic acid. If this is the case, the current of nitrous acid must immediately be stopped, because an excess of the acid would convert the required substance into other new products. The alcoholic solution, which is of a brownish-red colour, now contains, even if the operation has been conducted with the greatest care, besides diazo-amidobenzol, a

more or less considerable quantity of other products which are all generated by the action of nitrous acid upon aniline. They consist of phenylic acid, benzol, a new body to which I have given the name of nitrate of diazobenzol, nitrate and nitrite of aniline, and perhaps also some unchanged aniline. In order to get rid of these bodies, the whole of the brown alcoholic solution is poured into a large quantity of water, from which the greater part of the diazo-amidobenzol immediately separates as a brown oily liquid, which soon solidifies to a crystalline mass, whilst a smaller quantity is deposited from the water, on standing for some time, in the form of yellow crystals. The crystalline precipitate, together with the yellow crystals, is separated, by filtration, from the mother-liquor, which contains nearly all the bye-products. The crude diazo-amidobenzol remaining on the filter is first pressed between bibulous paper, in order to get rid of the last traces of the mother-liquor, then washed several times with cold alcohol, and, lastly, twice or three times recrystallised from boiling spirit, whereby it is obtained in golden yellow plates of perfect purity. On analysis it gave numbers agreeing with the formula :—



The formation of diazo-amidobenzol is represented by the following equation :—

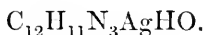


Properties.—Diazo-amidobenzol crystallises in golden yellow lustrous plates, rarely in needles. It is insoluble in water, rather easily soluble in hot, insoluble in cold alcohol. It is miscible with ether in every proportion. It melts at 91° , forming a reddish-brown oil, which resolidifies to a crystalline mass at about 50° . At a higher temperature it is decomposed, with rapid evolution of gas. If a larger quantity is heated up to 200° a violent explosion is the result. Diazo-amidobenzol is inodorous and tasteless. Weak acids are not capable of dissolving it, whilst powerful acids decompose it at once, with evolution of nitrogen. From this deportment it is evident that the well-defined basic properties of the aniline have been considerably modified by the replacement of its hydrogen by nitrogen. Diazo-amidobenzol is, in fact, no longer capable of forming with acids

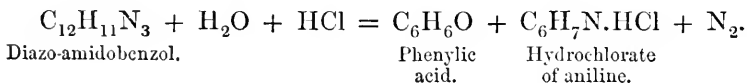
any saline compounds whatever, and only in its deportment with dichloride of platinum, with which it forms a double compound, does it show that its basic character has not entirely disappeared.

Platinum-salt of Diazo-amidobenzol. — $C_{12}H_{11}N_3.HCl.PtCl_2$. This salt is easily obtained by treating an alcoholic solution of diazo-amidobenzol with dichloride of platinum and hydrochloric acid, when it immediately separates in small reddish needles or prisms. They are thrown on a filter in order to get rid of the mother-liquor, and are rendered perfectly pure by thorough washing with alcohol. They are very unstable and are gradually decomposed in a moist atmosphere, apparently with formation of phenylic acid. They deflagrate at a high temperature; the platinum cannot therefore be determined by simple ignition.

Diazo-amidobenzol and Nitrate of Silver.—On mixing the alcoholic solutions of the two substances, a bulky, greenish-yellow precipitate is at once obtained, which on drying, shrinks together very much, and is very apt to blacken. Its composition is represented by the formula :

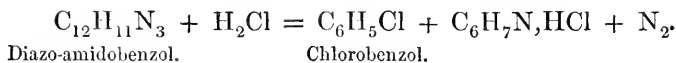


PRODUCTS OF DECOMPOSITION OF DIAZO-AMIDOBENZOL. — Decomposition by hydrochloric acid. When diazo-amidobenzol is warmed with concentrated hydrochloric acid, which has been covered with a layer of ether, two atoms of water are assimilated and take the place of two atoms of nitrogen, the substance at the same time splitting up as shown in the following equation :—



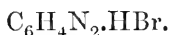
The hydrochlorate of aniline is found in the aqueous hydrochloric acid, whilst the phenylic acid is taken up by the ether. I have not analysed either the phenylic acid or the aniline, the presence of both bodies having been sufficiently established by their well-known properties. I have, however, quantitatively determined the amount of nitrogen evolved during the reaction. I obtained 13.67 p. c. of nitrogen. The preceding equation requires 14.21 p. c.

It is highly probable that diazo-amidobenzol under the influence of anhydrous hydrochloric acid would be decomposed thus :—

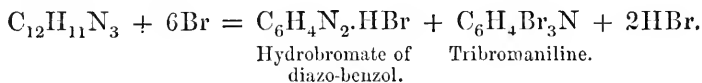


This decomposition would then be quite analogous to that of diazo-amidobenzoic acid by hydrochloric acid.

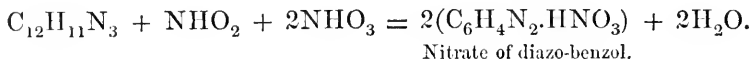
Action of Bromine upon Diazo-amidobenzol.—When a moderately concentrated ethereal solution of diazo-amidobenzol is treated with an ethereal solution of bromine, it will be observed that every addition of the bromine causes a fresh precipitate of small white plates. As soon as the addition of bromine no longer produces a precipitate, the white crystals must be rapidly separated from the mother-liquor by filtration, and washed with ether until they are perfectly white. The analysis of this substance which I shall communicate in my next paper, has proved it to be a compound of hydrobromic acid with a new body which I have called diazo-benzol. The formula of this hydrobromate is—



On evaporating the ethereal mother-liquor, from which that compound has separated, white needles begin to crystallise out, possessing all the properties of tribromaniline. The transformation of diazo-amidobenzol with bromine may be expressed by the following equation:—



Action of Nitrous Acid.—If diazo-amidobenzol be dissolved in a mixture of strong alcohol and ether, and then treated with nitrous acid, white crystals of nitric diazo-amidobenzol make their appearance; they are formed according to the following equation:—



I shall describe this reaction more minutely in a future paper.

In his researches on the substitution-products of aniline, Dr. Hofmann observed that the basic character of aniline is weakened in proportion to the amount of hydrogen replaced by bromine, chlorine, or hyponitric acid, so that, for instance, tribromaniline

becomes a perfectly indifferent body. The feebly basic properties of diazo-amidobenzol have proved that nitrogen also exerts an acidifying influence upon aniline, and even in a higher degree than chlorine or bromine. The task presented itself of ascertaining whether this phenomenon would also occur with bromaniline, nitraniline, &c., and whether the action of nitrous acid upon dibrom- and tribrom-aniline might not even give rise to bodies of a decidedly acid character.

In what degree this view has been confirmed by my researches I shall communicate hereafter. I will first of all make a few remarks upon chlorinated and brominated aniline themselves.

ON BROMINE AND CHLORINE SUBSTITUTION-PRODUCTS OF ANILINE.

According to the researches of Arppe,* the nitraniline which he obtained by the decomposition of pyrotartronitrilide by potash is not identical with that prepared by Muspratt and Hofmann by the reduction of dinitrobenzol with sulphide of ammonium. In order to distinguish the two compounds, Arppe has given to his own the name α -nitraniline, whilst that of Muspratt and Hofmann he has called β -nitraniline.

The chlorinated and brominated anilines were, as is well known, originally prepared by Hofmann from the corresponding chlorinated and brominated substitution-products of isatin.

Mills† has recently described a method for the preparation of these bodies which is preferable to that of Hofmann. It consists in converting acetanilide into brom- or chlor-acetanilide and then distilling these compounds with caustic potassa. Mills has left it undecided whether the substituted anilines thus prepared are identical with those of Hofmann, or whether they are isomeric, like the two nitranilines just mentioned.

The solution of this question was of the more interest to me as the fact of the nitrogen bodies to be obtained from the brom- or chlor-anilines being eventually isomeric or identical could have been decided beforehand. I have, therefore, carefully compared the properties of Mills's brom- and chlor-aniline with the compounds prepared according to Hofmann's method. I found such a perfect coincidence in the properties of the free bases, as

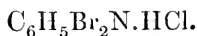
* Ann. Ch. Pharm. xciii. 357.

† Proceedings of the Royal Society.

well as of their salts, that I have no hesitation in pronouncing them to be identical. Bromaniline, according to Hofmann, melts at 50° C. I have, on the contrary, found that the melting point of bromaniline, purified by several recrystallisations, is 57° C. Neither could I confirm the observation made by Mills, that the bromaniline prepared according to his method has a greater tendency to crystallise in needles. When in a state of purity I have always obtained it crystallised in the form of octahedrons.

The same advantages, offered in the preparation of brom- and chlor-aniline according to Mills's method, hold good, as I have found, when preparing dibrom- and dichlor-aniline in a similar manner. In order, for this purpose, to convert the acetanilide into dibromacetanilide, it is suspended in water and treated with bromine until the whole of the acetanilide has been converted into a reddish resinous mass. The crude dibromacetanilide thus formed may at once, without separating the water, be submitted to distillation with potash, when the dibromaniline distils over in oily drops which soon solidify to white needles. It may be purified from any tribromaniline with which it is mixed, by dissolving in warm moderately concentrated hydrochloric acid, in which the latter substance is insoluble. If traces of bromaniline are present, the hydrochloric acid solution is evaporated to dryness and then treated with water. By this treatment the hydrochlorate of bromaniline suffers no alteration, whilst the dibromaniline loses its hydrochloric acid and becomes insoluble in water, and may, therefore, be completely purified from bromaniline by washing with water. Recrystallisation from dilute alcohol furnishes the dibromaniline in needles or long plates. Although its preparation and properties scarcely leave a doubt of its identity with the compound prepared according to Hofmann's method, I have yet determined the melting point of each of them and have found them to coincide at 79.5° C.*

The hydrochlorate also of the dibromaniline prepared by me, crystallised in the same shape, resembling palm-branches, as described by Hofmann. Analysis gave numbers agreeing with the formula:—



* Hofmann states the melting point of dibromaniline to lie between 50° and 60° C.

The feebly basic properties which dibromaniline possesses, are still manifest in its deportment with dichloride of platinum. A concentrated hydrochloric acid solution mixed with dichloride of platinum, yields a double salt crystallising in beautiful yellow prisms. This compound is very unstable and is decomposed even by hot water with separation of dibromaniline. Its formula is:—

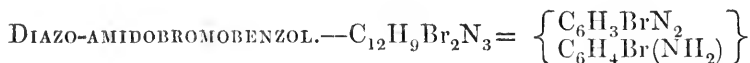


To prepare dichloraniline through the agency of acetanilide, the latter is dissolved in hot water and treated with an excess of chlorine until the crystalline mass which was first deposited has become quite soft. This crude dichloraniline is separated from the mother-liquor and distilled with potash. The distillate must be purified in the same manner as the dibromaniline.

Dichloraniline crystallises, like the corresponding bromine-compound, in white needles, which are nearly insoluble in water but are readily taken up by alcohol or ether. A substance which Hofmann supposed to be dichloraniline, was prepared by him from chlorinated isatin. He obtained it, together with chloraniline, in such minute quantity that he was unable to give a definite description of its properties, still less to determine its composition by an analysis. I have, on this account, treated the dichloraniline prepared by me, with dichloride of platinum, and have submitted the resulting double salt to analysis. Numbers were obtained corresponding with the formula—



This platinum-salt crystallises in yellow prisms, which are also readily decomposed by water, with separation of the base.



The preparation of this compound is much more easily accomplished than that of diazo-amidobenzol. On treating an alcoholic solution of bromaniline with nitrous acid, the diazo-amidobromobenzol separates after a short time in the form of yellow needles. They need only be once recrystallised from warm alcohol in order to render them perfectly pure for analysis.

Diazo-amidobromobenzol crystallises in yellowish-red, lustrous plates or needles, which are insoluble in water, difficultly soluble in alcohol, but very soluble in ether. Diazo-amidobromobenzol melts at 145°C . In its deportment it exhibits the closest analogy to diazo-amidobenzol, its resemblance to that body being even greater than that existing between bromaniline and aniline.

I have prepared this compound from bromaniline, obtained, not only according to Hofmann's method from bromisatin, but also from that made from bromacetanilide as proposed by Mills. No difference could be detected between the diazo-amidobromobenzols obtained from the bromanilines prepared according to the two different methods.

Platinum-salt of Diazo-amidobromobenzol.—On mixing an alcoholic solution of diazo-amidobromobenzol with dichloride of platinum, this salt separates in the form of pale-yellow hair-like crystals which are nearly insoluble in water, alcohol, and ether. On the application of heat, they deflagrate, leaving a woolly mass of platinum and carbon.

Diazo-amidochlorobenzol.— $\text{C}_{12}\text{H}_9\text{Cl}_2\text{N}_3$.

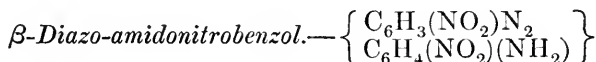
It is obtained from chloraniline and forms yellow needles or plates greatly resembling the preceding compound. I have only determined their melting point; it lies at 124.5°C .

α -Diazo-amidonitrobenzol, $\text{C}_{12}\text{H}_9(\text{NO}_2)_2\text{N}_3 = \begin{cases} \text{C}_6\text{H}_3(\text{NO}_2) \\ \text{C}_6\text{H}_4(\text{NO}_2) \end{cases}$

$\left. \begin{matrix} \text{N}_2 \\ (\text{NH}_2) \end{matrix} \right\}$ The preparation of this body is also extremely simple.

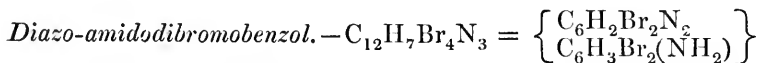
Alpha-nitraniline is dissolved in a moderate quantity of cold alcohol, and on passing nitrous acid into the solution, the new compound separates after a short time as a yellow crystalline mass. When separated from the mother-liquor and washed with cold alcohol, it is perfectly pure for analysis. The α -diazo-amidonitrobenzol is precipitated, as I have stated, as a yellow crystalline mass in which no distinct form of crystallisation can be recognised. Generally it consists of an agglomeration of granular or mossy microscopic particles. Even by recrystallisation from alcohol it is seldom obtained in a decided form; only once have I succeeded in obtaining yellow needle-shaped crystals, whose planes exhibited a beautiful violet lustre. α -diazo-amidonitrobenzol is insoluble in water, very difficultly soluble even in boiling alcohol

and ether. It melts at $224\cdot5^{\circ}$ C. to a reddish-brown oil. At a higher temperature it deflagrates, diffusing at the same time an aromatic odour. It is an almost perfectly indifferent substance. I could not even succeed in preparing a compound with dichloride of platinum; nitrate of silver, however, still gives, even in very dilute alcoholic solutions, a yellowish-green amorphous precipitate.



When β -nitraniline is submitted to the action of nitrous acid, almost exactly the same phenomena are observed as those which occur in the preparation of the preceding compound. The crystals which have been deposited, but which in this case exhibit a perfectly distinct form, are easily purified in the same manner.

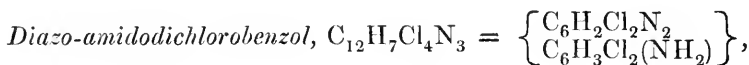
The β -diazo-amidonitrobenzol differs only in a few points from the α compound. It is equally insoluble in water, and appears also to be as difficultly soluble in alcohol and ether. The two substances also seem to agree in their deportment with reagents, as far as could be decided by preliminary experiments. On the other hand, the melting point of β -diazo-amidonitrobenzol is $195\cdot5^{\circ}$ C., consequently 29° lower than that of α -diazo-amidonitrobenzol. The α compound crystallises as a rule in granular or moss-like shapes, whilst the β -diazo-amidonitrobenzol separates already during its preparation, in small though generally well-defined, ruby or reddish-yellow prisms, which by recrystallisation from alcohol or ether may be obtained of a considerable size.



On passing a current of nitrous acid gas into a very dilute alcoholic solution of dibromaniline, the diazo-amidodibromobenzol is obtained as a bulky light-yellow precipitate. Repeated washing with alcohol renders it perfectly pure.

Diazo-amidodibromobenzol has a great tendency to crystallise in different forms. From alcohol and ether, in which it is very difficultly soluble, even at the boiling temperature, it crystallises in fine golden-yellow interlaced needles, which melt at $167\cdot5^{\circ}$ C., but deflagrate at a higher temperature. On allowing an alcoholic

solution to evaporate spontaneously, yellowish-brown granules are frequently obtained which show a golden-yellow fracture and a radiating crystalline structure. On several occasions, and under conditions not accurately determined, α -diaz-amidodibromobenzol, prepared from not absolutely pure dibromaniline crystallised from ether in extraordinarily beautiful yellow or ruby well-defined prisms. As this form, differing in such a characteristic manner from the yellow needles, appertained to the dibromaniline obtained from dibromisatin, I should have been inclined, in spite of what I had previously stated in regard to dibromaniline, to seek the cause of this difference in the dibromaniline prepared by the different methods. I soon, however, convinced myself, that the beautiful red crystals are converted, on further re-crystallisation from ether, into the same golden-yellow hair-like needles.



is also prepared from dichloraniline and crystallises also in hair-like needles, which are, however, distinguished from the bromine compound by their light sulphur-yellow colour. It is insoluble in water, and very difficultly soluble in boiling alcohol and ether. It melts at $126.5^\circ C$.

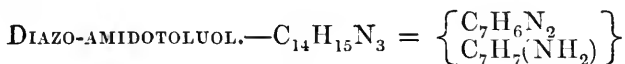
In their deportment with reagents, diazo-amidodibromobenzol and diazo-amidodichlorobenzol exhibit the greatest analogy to the nitrogen-substituted aniline-derivatives already described, whilst under the same conditions they yield corresponding products of decomposition. They also form precipitates with nitrate of silver. Their basic character, however, has completely disappeared; they no longer give platinum-salts; in fact, they possess more the character of an acid than that of a base, as they dissolve with ease in alcoholic potash, forming a reddish-brown solution, from which the original substance is precipitated in a perfectly unaltered state on the addition of an acid. It is, however, not possible to prepare salts of a definite composition. Aqueous potash has no action upon these bodies.

From what has been stated it is obvious that the acidifying influence exerted by nitrogen, when taking the place of hydrogen in aniline, is repeated in an equal degree with the substitution-products of that body.

If aniline and its bromine, hyponitric acid and other derivatives, be arranged in the order of their basic properties, there may be placed opposite to every individual of this series, a diazo double compound, the basic properties of which differ from the basic properties of the corresponding aniline body by the acidifying value of one atom of nitrogen.

If the diazo-amidodibromobenzol corresponding to dibromaniline already exhibited distinct acid properties, it was to be expected that a body of a perfectly acid character would be obtained by the action of nitrous acid upon tribromaniline. I have instituted many experiments in order to obtain such a body, but without success. Nitrous acid has not, under any circumstances, the slightest action upon tribromaniline.

Although it was to be expected that the researches conducted with the aniline group, described in the preceding pages, would, when repeated with bases of analogous composition, lead to corresponding results, I have not omitted to prove this analogy by experiment.



In order to prepare this body, toluidine (amidotoluol) is dissolved in a small quantity of strong alcohol and the solution is mixed with two or three times its volume of ether. After passing nitrous acid for a short time, the originally nearly colourless solution assumes a yellow colour. A drop of the solution is now taken out and evaporated on a watch-glass; if it leaves a residue of yellow needles, the operation is stopped, and the mixture of alcohol and ether is allowed to evaporate spontaneously. Yellow needle-shaped crystals are deposited, which must be washed with alcohol and then recrystallised from alcohol and ether. When dried over sulphuric acid and submitted to analysis, they gave numbers leading to the formula

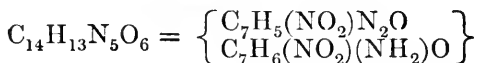


Diazo-amidotoluol crystallises in yellow or reddish-yellow needles or prisms possessing a powerful lustre, and corresponding, in their solubility as well as in every other relation, with diazo-amidobenzol.

Platinum-salt of Diazo-amidotoluol, $\text{C}_{14}\text{H}_{15}\text{N}_3 \cdot 2\text{HCl} \cdot 2\text{PtCl}_2$. It

is obtained in yellow glittering plates resembling iodide of lead, on mixing an alcoholic solution of diazo-amidotoluol with dichloride of platinum. It deflagrates at a high temperature.

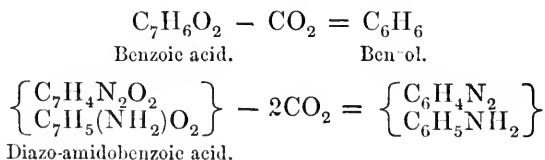
DIAZO-AMIDONITRANISOL.



This body falls in small yellow crystals on passing nitrous acid into a dilute alcoholic solution of nitranisidine* [amidonitranisol = $\text{C}_7\text{H}_6(\text{NO}_2)(\text{NH}_2)\text{O}$]. It forms microscopic yellow needles, insoluble in water, difficultly soluble in hot alcohol and ether. When dry they are rendered highly electric by friction. They melt, on the application of heat, to a reddish-brown oil, and deflagrate on raising the temperature. Diazo-amidonitranisol, under the influence of reagents, appears to undergo changes similar to those of its representatives in the aniline group.

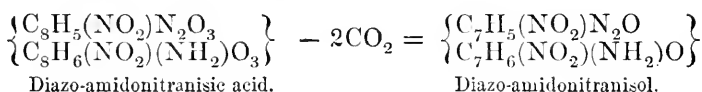
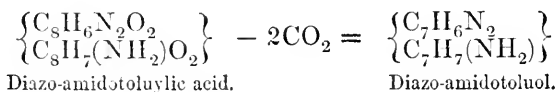
On referring once more to the most characteristic points of the nitrogen substitution-products of the hydrocarbons of the aromatic series, it will be observed that, not only in their formation, but also in their properties and decompositions, they correspond in every relation with the peculiarities of that series of acids of which the best studied individual is diazo-amidobenzoic acid. This is but natural, as all the transformations which benzoic acid and its homologues undergo, under the influence of substitution processes, are also effected in the hydrocarbons which in combination with CO_2 form the corresponding aromatic acids.

In the same measure as benzoic acid on distillation with baryta yields carbonic acid and benzol, or as amidobenzoic acid splits up into carbonic acid and amidobenzol, so, doubtless, would diazo-amidobenzol be obtained from diazo-amidobenzoic acid under similar conditions, if the instability of this compound did not preclude every possibility of its formation under such circumstances.



* The nitranisidine was obtained from dinitranisol, which was prepared according to Cahour's method from nitranisic acid.

The following compounds stand in the same relation :—



In a preliminary note on these bodies I referred them to the type $\left. \begin{array}{l} \text{H}_2 \\ \text{H}_2 \\ \text{H}_2 \end{array} \right\} \text{N}_2$. This was done at a time when I knew but little of their products of decomposition. If, after the observations communicated in this paper, diazo-amidobenzol, for instance, were still to

be considered as a diamine, having the formula $\left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \\ \text{N}'''' \\ \text{H} \end{array} \right\} \text{N}_2$, on

endeavouring to explain the phenomena of its decompositions, the same inconsistencies would become apparent, as when supposing diazo-amidobenzoic acid to be constituted according to the rational formula $\left[(\text{C}_7\text{H}_4\text{O})''\text{HN}'''' \right]_{\text{H}_2}^{\text{viii} \text{N}_2} \text{O}_2$.

IX.—*Action of Heat on Ferric Hydrate in presence of Water.*

By EDWARD DAVIES, F.C.S., Liverpool.

HAVING noticed the occurrence of shining particles, apparently crystalline, in precipitated ferric oxide which had been boiled for a considerable time, I made the following experiments with a view to ascertain if the oxide could be obtained in the anhydrous state by boiling with water. Being aware that M. Péan de St. Gilles has investigated the properties of the oxide thus altered, I confined myself to the determination of the amount of water. In the memoir above cited the oxide is spoken of as being a hydrate; it appears, however, that it is for the most part anhydrous. In the following experiments the ferric hydrate was prepared from ferric

chloride. This was made by twice crystallising the ferrous chloride, passing chlorine through a dilute solution, and removing excess of chlorine by heating gently for some time.

The water was determined by careful ignition, the absence of chlorine being proved by mixing a portion of the oxide with pure carbonate of sodium, moistening with distilled water, drying and gently igniting. The mass was boiled with water, and on testing the solution only a very faint trace of chlorine was in any case detected.

1. Some solution of ferric chloride was precipitated by ammonia, the precipitate thoroughly washed with boiling water, and then boiled with distilled water for 112 hours, loss by evaporation being prevented by a condensing apparatus. The oxide became dense and lost its gelatinous appearance. It was again washed, and dried at 100° C. On ignition—

17·85 grains lost 1·03 grain, or 5·77 %

* $\text{Fe}_2\text{O}_3\text{H}_2\text{O}$ contains 10·11 %.

2. The solution was precipitated as before and then boiled 100 hours without filtering from the chloride of ammonium, thoroughly washed and dried at 100° C.

13·805 grain lost ·56 grain, or 4·05 %.

3. On using hydrate of potassium in slight excess, and treating as in No. 2, not filtering, and boiling for 100 hours, the dehydration was not so complete, contrary to expectation, as the oxide in the former cases contained traces, not to be estimated, of ammonia.

25·77 grains lost 1·69 grains, or 6·55 %.

4. Fearing that the loss might take place during the drying, a portion of washed oxide was dried at 100° C. for at least an equal time, being finely pulverised when dry, and finally heated until it no longer lost weight after several hours' interval.

15·64 grains lost 1·43 grains, or 9·14 %,

being slightly below one equivalent.

5. Boiling the oxide for long periods being inconvenient on

* Fe = 56.

account of the bumping which occurs when the oxide has undergone the physical change, I resolved to try the effect of gently heating for a very prolonged period. The oxide was precipitated in the cold by ammonia, washed with cold water and heated for 1004 hours at a temperature varying from $50-60^{\circ}$ C., with frequent agitation. In a few days it became dense, and brick-red in colour. It was washed with water at 50° C., and dried at the same temperature.

20.50 grains lost .84 grain, or 4.09 %.

6. As the oxide in No. 5 contained a trace of ammonia, hydrate of sodium was substituted as a precipitant, the oxide was washed as before, heated at $50-60^{\circ}$ C. for 2,000 hours. The flask was closed and heated in an oil-bath.

38.46 grains lost 1.75 grains, or 4.55 %.

19.20 .90 grain, or 4.68 %.

It thus appears to be impossible to drive off all the water, 4 to 5 per cent. adhering with extraordinary tenacity.

The oxide thus prepared is brick-red, very dense, having a specific gravity of 4.545, that of red hæmatite being 4.7. It dissolves very slowly in nitric acid, more readily in hydrochloric acid. Under the microscope the dried oxide presents angular masses, translucent when very thin. Hoping to remove the unchanged hydrate with nitric acid, 24.18 grains of oxide prepared as in No. 6 were heated to 50° C. for one hour with 2 oz. of dilute nitric acid (1 part acid to 3 parts water). 4.77 grains dissolved, and the residue was washed until no longer acid, and dried at 50° C.

18.48 grains lost .65 or 3.517 %.

These experiments show that the immense beds of hæmatite found in our own and other countries do not demand the supposition of great heat, to account for their anhydrous state. Probably much lower temperatures than that employed in the foregoing experiments, acting in presence of water for a long period would bring about the same change.

The various statements respecting the amount of water in ferric hydrate are thus explained, that amount depending on the length of time during which the hydrate was exposed to the action of water, and a more or less elevated temperature.

Chromic and aluminic hydrates were also operated upon by precipitating them with ammonia, washing and boiling for 100 hours. No action appeared to take place, aluminic hydrate retaining 3 eqs. of water, and chromic hydrate 5 eqs. The hydrates retained their gelatinous condition.

X.—*Tables for the Calculation of Vapour-density Determinations.*

By JAS. T. BROWN.

If under the head of vapours we include gases, there are several tables which may be used for lessening the labour of calculating a vapour-density. There is one by Gerhardt* giving approximately the values of the expression $760 (1 + 0.00367 T)$ for every integral value of T from 0 to 30. There is another by Bunsen† indicating the values of $1 + 0.00366 T$ and $\log. (1 + 0.00366 T)$ for every $T = 0.1$ from -2 to $+40$. There is also a table calculated by Mr. Greville Williams, giving the values of the formula $\frac{1}{1 + 0.00367 T}$ for every $T = 1$ from 0 to 150; and lastly Gerhardt‡ gives the values of $\log. (1 + 0.00367 T)$ for every integral value of T from 0 to 299. But I found that by substituting the weight of a cubic centimetre of air for that of a cubic centimetre of nitrogen in the formula with which I headed a table for the calculation of direct nitrogen determinations, I obtained an expression which occurs three times in the formula for the determination of a vapour-density according to the method of Dumas. For in this formula, which is generally written—

$$D = \frac{P' - P + p - p'}{0.0012932 \left[V \left(1 + k (T - t) \right) - v' \right] \frac{1}{1 + 0.00367 T} \times \frac{H}{760}}$$

but which, written without any abbreviation and modified, becomes

* Gerhardt, *Traité de Chimie Organique*, vol 1, page 50.

† Bunsen's *Gasometry*, translated by Roscoe, page 268.

‡ Gerhardt, vol 1, page 115.

$$D = \frac{P' - P + \left(\frac{0.0012932}{760(1 + 0.00367t)} \times V \times H \right) - \left(\frac{0.0012932}{760(1 + 0.00367t)} \times v \times H \right)}{\left[V(1 + k(T - t)) - v \left(1 + \frac{0.00367}{1 + 0.00367t}(T - t) \right) \right] \frac{0.0012932}{760(1 + 0.00367T)} \times H}$$

we see the repetition of the expression $\frac{0.0012932}{760(1 + 0.00367T)}$. From this expression I have calculated a table of its values for every $T = 0.5$ from -20 to $+50$ and for every $T = 1$ from 51 to 350 . I have also added a column of differences for calculating the fractional values of the expression. In order to find the weight, in grammes, of a given volume of air, at any pressure and temperature up to 350°C. , multiply the number in the table headed $\frac{0.0012932}{760(1 + 0.00367T)}$ corresponding to the temperature by the volume expressed in cubic centimetres, and also by the pressure expressed in millimetres.

In substituting $\left[\left(1 + \frac{0.00367}{1 + 0.00367t}(T - t) \right) \right]$ for $\frac{1 + 0.00367T}{1 + 0.00367t}$, I have made no actual alteration, as the two expressions are equal; but, as I have given a table indicating the values of the quantity $\frac{0.00367}{1 + 0.00367t}$ for every $t = 0.5$ from -20 to $+50$, the expression is reduced to the simple form of $1 + k(T - t)$. In calculating by this table, it is only necessary to use it to the fifth decimal place, unless the value of v is very large.

In calculating the table for correcting for the expansion of the glass, viz., that headed $1 + k(T - t)$ I have adopted the values of k as given by Regnault*, taking the average value of t at 20 . Gerhardt gives a table, for the same purpose, headed $\log. [1 + k(T - t)]$ for every $T - t = 10$ from 100 to 290 and takes the value of k at 0.000027 .

The three following examples will illustrate more fully the use of the tables.

Ex. 1.—To find the weight of 90 c.c. of air at a temperature of 15°C. , and at a pressure of 746 mm.

$$0.00000161279 \times 90 \times 746 = 0.108282 \text{ gramme.}$$

Ex. 2.—To find the density of a vapour from the following data (Dumas).

* Regnault's *Elements of Chemistry*, translated by Betton, vol 2, page 420.

† Gerhardt, vol 1, page 117.

$$T = 350^{\circ} \text{ C.} \quad T - t = 335$$

$$t = 15^{\circ} \text{ C.}$$

$$P' = 28.3920 \text{ grammes.}$$

$$P = 28.2093 \quad ,,$$

$$V = 90 \text{ c. c.}$$

$$v = 0.5 \text{ c. c.}$$

$$H = 746 \text{ mm.}$$

$$D = \frac{28.3920 - 28.2093 + (0.0000016127 \times 90 \times 746) - (0.000001612 \times 0.5 \times 746)}{[90(1.0104) - 0.5(1 + 0.00347 \times 335)] \times 0.0000007448 \times 746}$$

$$= \frac{28.3920 - 28.2093 + 0.1082 - 0.0006}{0.0499} = \frac{0.2903}{0.0499} = 5.81$$

Ex. 3.—To find the density of a vapour from the following data (Gay-Lussac)—

$$D = \frac{P}{\frac{0.0012932}{760(1 + 0.00367T)} + V \times H'}$$

$$P = 0.1069.$$

$$V = 43 \text{ c. c.}$$

$$H = 761 \text{ mm.; } H' = 680.5.$$

$$\text{Diff. of level} = 80.5 \text{ mm.}$$

$$T = 96.$$

$$D = \frac{0.1069}{0.0000012582 \times 43 \times 680.5} = \frac{0.1069}{0.03681} = 2.904$$

T	$\frac{0.0012932}{760(1 + 0.00367T)}$	Diff.	t	$\frac{0.00367}{1 + 0.00367t}$	Diff.
-20	0.00000183636	363	-20	0.00396071	783
-19.5	0.00000183273	361	-19.5	0.00395288	779
-19	0.00000182912	360	-19	0.00394509	777
-18.5	0.00000182552	359	-18.5	0.00393732	774
-18	0.00000182193	357	-18	0.00392958	770
-17.5	0.00000181836	356	-17.5	0.00392188	768
-17	0.00000181480	355	-17	0.00391420	764
-16.5	0.00000181125	353	-16.5	0.00390656	762
-16	0.00000180772	351	-16	0.00389894	758
-15.5	0.00000180421	351	-15.5	0.00389136	756
-15	0.00000180070	349	-15	0.00388380	753
-14.5	0.00000179721	347	-14.5	0.00387627	750
-14	0.00000179374	347	-14	0.00386877	747
-13.5	0.00000179027	345	-13.5	0.00386130	744
-13	0.00000178682	343	-13	0.00385386	741
-12.5	0.00000178339	343	-12.5	0.00384645	738
-12	0.00000177996	341	-12	0.00383907	736
-11.5	0.00000177655	339	-11.5	0.00383171	732

T	0.0012932	Diff.	<i>t</i>	0.00367	Diff.
	$760(1 + 0.00367T)$			$1 + 0.00367t$	
-11	0.00000177316	339	-11	0.00382439	730
-10.5	0.00000176977	337	-10.5	0.00381709	727
-10	0.00000176640	336	-10	0.00380982	725
-9.5	0.00000176304	334	-9.5	0.00380257	721
-9	0.00000175970	334	-9	0.00379536	719
-8.5	0.00000175636	332	-8.5	0.00378817	716
-8	0.00000175304	330	-8	0.00378101	714
-7.5	0.00000174974	330	-7.5	0.00377387	711
-7	0.00000174644	328	-7	0.00376676	708
-6.5	0.00000174316	327	-6.5	0.00375968	705
-6	0.00000173989	326	-6	0.00375263	703
-5.5	0.00000173663	325	-5.5	0.00374560	700
-5	0.00000173338	323	-5	0.00373860	698
-4.5	0.00000173015	322	-4.5	0.00373162	695
-4	0.00000172693	321	-4	0.00372467	692
-3.5	0.00000172372	320	-3.5	0.00371775	690
-3	0.00000172052	319	-3	0.00371085	687
-2.5	0.00000171733	317	-2.5	0.00370398	685
-2	0.00000171416	317	-2	0.00369713	682
-1.5	0.00000171099	315	-1.5	0.00369031	680
-1	0.00000170784	314	-1	0.00368351	677
-0.5	0.00000170470	313	-0.5	0.00367674	674
0	0.00000170157	311	0	0.00367000	673
+ 0.5	0.00000169846	311	+ 0.5	0.00366327	669
1	0.00000169535	309	1	0.00365658	668
1.5	0.00000169226	308	1.5	0.00364990	665
2	0.00000168918	308	2	0.00364325	662
2.5	0.00000168610	306	2.5	0.00363663	660
3	0.00000168304	305	3	0.00363003	658
3.5	0.00000167999	303	3.5	0.00362345	655
4	0.00000167696	303	4	0.00361690	653
4.5	0.00000167393	302	4.5	0.00361037	651
5	0.00000167091	300	5	0.00360386	648
5.5	0.00000166791	300	5.5	0.00359738	646
6	0.00000166491	298	6	0.00359092	643
6.5	0.00000166193	297	6.5	0.00358449	642
7	0.00000165896	297	7	0.00357807	639
7.5	0.00000165599	295	7.5	0.00357168	636
8	0.00000165304	294	8	0.00356532	635
8.5	0.00000165010	293	8.5	0.00355897	632
9	0.00000164717	292	9	0.00355265	630
9.5	0.00000164425	291	9.5	0.00354635	628
10	0.00000164134	290	10	0.00354007	625
10.5	0.00000163844	289	10.5	0.00353382	623
11	0.00000163555	288	11	0.00352759	621
11.5	0.00000163267	287	11.5	0.00352138	619
12	0.00000162980	286	12	0.00351519	617
12.5	0.00000162694	285	12.5	0.00350902	615
13	0.00000162409	284	13	0.00350287	612
13.5	0.00000162125	283	13.5	0.00349675	610
14	0.00000161842	282	14	0.00349065	609
14.5	0.00000161560	281	14.5	0.00348456	606
15	0.00000161279	280	15	0.00347850	604
15.5	0.00000160999	279	15.5	0.00347246	601
16	0.00000160720	278	16	0.00346645	600
16.5	0.00000160442	277	16.5	0.00346045	598

T	0.0012932	Diff.	<i>t</i>	0.00367	Diff.
	$760(1 + 0.00367T)$			$1 + 0.00367t$	
17	0.00000160165	276	17	0.00345447	596
17.5	0.00000159889	276	17.5	0.00344851	593
18	0.00000159613	274	18	0.00344258	592
18.5	0.00000159339	273	18.5	0.00343666	589
19	0.00000159066	273	19	0.00343077	588
19.5	0.00000158793	271	19.5	0.00342489	585
20	0.00000158522	271	20	0.00341904	584
20.5	0.00000158251	269	20.5	0.00341320	581
21	0.00000157982	269	21	0.00340739	580
21.5	0.00000157713	268	21.5	0.00340159	577
22	0.00000157445	267	22	0.00339582	577
22.5	0.00000157178	266	22.5	0.00339005	573
23	0.00000156912	265	23	0.00338432	571
23.5	0.00000156647	264	23.5	0.00337861	570
24	0.00000156383	263	24	0.00337291	568
24.5	0.00000156120	263	24.5	0.00336723	566
25	0.00000155857	261	25	0.00336157	564
25.5	0.00000155596	261	25.5	0.00335593	562
26	0.00000155335	260	26	0.00335031	560
26.5	0.00000155075	258	26.5	0.00334471	559
27	0.00000154817	258	27	0.00333912	556
27.5	0.00000154559	258	27.5	0.00333356	555
28	0.00000154301	256	28	0.00332801	553
28.5	0.00000154045	255	28.5	0.00332248	551
29	0.00000153790	255	29	0.00331697	549
29.5	0.00000153535	254	29.5	0.00331148	548
30	0.00000153281	253	30	0.00330600	545
30.5	0.00000153028	252	30.5	0.00330055	544
31	0.00000152776	251	31	0.00329511	542
31.5	0.00000152525	251	31.5	0.00328969	540
32	0.00000152274	249	32	0.00328429	539
32.5	0.00000152025	249	32.5	0.00327890	536
33	0.00000151776	243	33	0.00327354	535
33.5	0.00000151528	247	33.5	0.00326819	533
34	0.00000151281	247	34	0.00326286	532
34.5	0.00000151034	245	34.5	0.00325754	530
35	0.00000150789	245	35	0.00325224	528
35.5	0.00000150544	244	35.5	0.00324696	526
36	0.00000150300	243	36	0.00324170	524
36.5	0.00000150057	243	36.5	0.00323646	523
37	0.00000149814	542	37	0.00323123	522
37.5	0.00000149572	240	37.5	0.00322601	519
38	0.00000149332	241	38	0.00322082	518
38.5	0.00000149091	239	38.5	0.00321564	516
39	0.00000148852	238	39	0.00321048	515
39.5	0.00000148614	238	39.5	0.00320533	513
40	0.00000148376	237	40	0.00320020	511
40.5	0.00000148139	237	40.5	0.00319509	509
41	0.00000147902	235	41	0.00319000	508
41.5	0.00000147667	235	41.5	0.00318492	507
42	0.00000147432	234	42	0.00317985	505
42.5	0.00000147198	233	42.5	0.00317480	503
43	0.00000146965	233	43	0.00316977	501
43.5	0.00000146732	232	43.5	0.00316476	500
44	0.00000146500	231	44	0.00315976	499
44.5	0.00000146269	230	44.5	0.00315477	497

T	0.0012932	Diff.	t	0.00337	Diff.
	$760(1 + 0.00367T)$			$1 + 0.00367t$	
45	0.00000146039	230	45	0.00314980	495
45.5	0.00000145809	229	45.5	0.00314485	494
46	0.00000145580	228	46	0.00313991	492
46.5	0.00000145352	227	46.5	0.00313499	490
47	0.00000145125	227	47	0.00313009	490
47.5	0.00000144898	226	47.5	0.00312519	487
48	0.00000144672	225	48	0.00312032	486
48.5	0.00000144447	225	48.5	0.00311546	485
49	0.00000144222	224	49	0.00311061	483
49.5	0.00000143998	223	49.5	0.00310578	481
50	0.00000143775		50	0.00310097	

T	0.0012932	Diff.	T	0.0012932	Diff.
	$760(1 + 0.00367T)$			$760(1 + 0.00367T)$	
51	0.00000143330	442	88	0.00000128619	356
52	0.00000142888	439	89	0.00000128263	354
53	0.00000142449	436	90	0.00000127909	352
54	0.00000142013	434	91	0.00000127557	350
55	0.00000141579	431	92	0.00000127207	348
56	0.00000141148	428	93	0.00000126859	346
57	0.00000140720	426	94	0.00000126513	344
58	0.00000140294	423	95	0.00000126169	343
59	0.00000139871	421	96	0.00000125826	340
60	0.00000139450	418	97	0.00000125486	339
61	0.00000139032	416	98	0.00000125147	337
62	0.00000138616	413	99	0.00000124810	335
63	0.00000138203	410	100	0.00000124475	333
64	0.00000137793	409	101	0.00000124142	332
65	0.00000137384	406	102	0.00000123810	330
66	0.00000136978	403	103	0.00000123480	328
67	0.00000136575	401	104	0.00000123152	326
68	0.00000136174	399	105	0.00000122826	324
69	0.00000135775	396	106	0.00000122502	323
70	0.00000135379	395	107	0.00000122179	321
71	0.00000134984	391	108	0.00000121858	320
72	0.00000134593	390	109	0.00000121538	318
73	0.00000134203	387	110	0.00000121220	316
74	0.00000133816	385	111	0.00000120904	314
75	0.00000133431	383	112	0.00000120590	313
76	0.00000133048	381	113	0.00000120277	311
77	0.00000132667	379	114	0.00000119966	310
78	0.00000132288	376	115	0.00000119656	308
79	0.00000131912	374	116	0.00000119348	306
80	0.00000131538	372	117	0.00000119042	305
81	0.00000131166	370	118	0.00000118737	303
82	0.00000130796	368	119	0.00000118434	302
83	0.00000130428	366	120	0.00000118132	300
84	0.00000130062	364	121	0.00000117832	299
85	0.00000129698	362	122	0.00000117533	297
86	0.00000129336	360	123	0.00000117236	296
87	0.00000128976	357	124	0.00000116940	294

T	$\frac{0.0012932}{760(1 + 0.00367T)}$	Diff.	T	$\frac{0.0012932}{760(1 + 0.00367T)}$	Diff.
125	0.00000116646	293	180	0.00000102467	226
126	0.00000116353	291	181	0.00000102241	225
127	0.00000116062	290	182	0.00000102016	224
128	0.00000115772	288	183	0.00000101792	223
129	0.00000115484	287	184	0.00000101569	222
130	0.00000115197	286	185	0.00000101347	221
131	0.00000114911	284	186	0.00000101126	220
132	0.00000114627	283	187	0.00000100906	219
133	0.00000114344	281	188	0.00000100687	218
134	0.00000114063	280	189	0.00000100469	217
135	0.00000113783	278	190	0.00000100252	217
136	0.00000113505	278	191	0.00000100035	215
137	0.00000113227	275	192	0.00000099820	215
138	0.00000112952	275	193	0.00000099605	213
139	0.00000112677	273	194	0.00000099392	213
140	0.00000112404	272	195	0.00000099179	211
141	0.00000112132	270	196	0.00000098968	211
142	0.00000111862	270	197	0.00000098757	210
143	0.00000111592	268	198	0.00000098547	209
144	0.00000111324	266	199	0.00000098338	208
145	0.00000111058	266	200	0.00000098130	207
146	0.00000110792	264	201	0.00000097923	207
147	0.00000110528	263	202	0.00000097716	205
148	0.00000110265	261	203	0.00000097511	205
149	0.00000110004	261	204	0.00000097306	204
150	0.00000109743	259	205	0.00000097102	203
151	0.00000109484	258	206	0.00000096899	202
152	0.00000109226	256	207	0.00000096697	201
153	0.00000108970	256	208	0.00000096496	201
154	0.00000108714	254	209	0.00000096295	199
155	0.00000108460	253	210	0.00000096096	199
156	0.00000108207	252	211	0.00000095897	198
157	0.00000107955	251	212	0.00000095699	197
158	0.00000107704	250	213	0.00000095502	196
159	0.00000107454	248	214	0.00000095306	196
160	0.00000107206	247	215	0.00000095110	194
161	0.00000106959	247	216	0.00000094916	194
162	0.00000106712	245	217	0.00000094722	193
163	0.00000106467	244	218	0.00000094529	193
164	0.00000106223	242	219	0.00000094336	191
165	0.00000105981	242	220	0.00000094145	191
166	0.00000105739	240	221	0.00000093954	190
167	0.00000105499	240	222	0.00000093764	190
168	0.00000105259	239	223	0.00000093574	188
169	0.00000105020	237	224	0.00000093386	188
170	0.00000104783	236	225	0.00000093198	187
171	0.00000104547	236	226	0.00000093011	186
172	0.00000104311	234	227	0.00000092825	185
173	0.00000104077	233	228	0.00000092640	185
174	0.00000103844	232	229	0.00000092455	184
175	0.00000103612	231	230	0.00000092271	183
176	0.00000103381	230	231	0.00000092088	183
177	0.00000103151	229	232	0.00000091905	182
178	0.00000102922	228	233	0.00000091723	181
179	0.00000102694	227	234	0.00000091542	180

T	$\frac{0.0012932}{760(1 + 0.00367T)}$	Diff.	T	$\frac{0.0012932}{760(1 + 0.00367T)}$	Diff.
235	0.00000091362	180	290	0.00000082428	146
236	0.00000091182	179	291	0.00000082282	146
237	0.00000091003	178	292	0.00000082136	145
238	0.00000090825	178	293	0.00000081991	145
239	0.00000090647	176	294	0.00000081846	144
240	0.00000090471	177	295	0.00000081702	144
241	0.00000090294	175	296	0.00000081558	143
242	0.00000090119	175	297	0.00000081415	143
243	0.00000089944	174	298	0.00000081272	142
244	0.00000089770	174	299	0.00000081130	141
245	0.00000089596	172	300	0.00000080989	142
246	0.00000089424	173	301	0.00000080847	140
247	0.00000089251	171	302	0.00000080707	141
248	0.00000089080	171	303	0.00000080566	139
249	0.00000088909	170	304	0.00000080427	140
250	0.00000088739	170	305	0.00000080287	138
251	0.00000088569	169	306	0.00000080149	139
252	0.00000088400	168	307	0.00000080010	138
253	0.00000088232	167	308	0.00000079872	137
254	0.00000088065	167	309	0.00000079735	137
255	0.00000087898	167	310	0.00000079598	136
256	0.00000087731	165	311	0.00000079462	136
257	0.00000087566	165	312	0.00000079326	136
258	0.00000087401	165	313	0.00000079190	135
259	0.00000087236	164	314	0.00000079055	134
260	0.00000087072	163	315	0.00000078921	134
261	0.00000086909	162	316	0.00000078787	134
262	0.00000086747	162	317	0.00000078653	133
263	0.00000086585	162	318	0.00000078520	133
264	0.00000086423	161	319	0.00000078387	132
265	0.00000086262	160	320	0.00000078255	132
266	0.00000086102	159	321	0.00000078123	131
267	0.00000085943	159	322	0.00000077991	131
268	0.00000085784	159	323	0.00000077860	130
269	0.00000085625	158	324	0.00000077730	130
270	0.00000085467	157	325	0.00000077600	130
271	0.00000085310	157	326	0.00000077470	129
272	0.00000085153	156	327	0.00000077341	129
273	0.00000084997	155	328	0.00000077212	128
274	0.00000084842	155	329	0.00000077084	128
275	0.00000084687	155	330	0.00000076956	128
276	0.00000084532	153	331	0.00000076828	127
277	0.00000084379	154	332	0.00000076701	127
278	0.00000084225	152	333	0.00000076574	126
279	0.00000084073	153	334	0.00000076448	126
280	0.00000083920	151	335	0.00000076322	125
281	0.00000083769	151	336	0.00000076197	125
282	0.00000083618	151	337	0.00000076072	125
283	0.00000083467	150	338	0.00000075947	124
284	0.00000083317	149	339	0.00000075823	124
285	0.00000083168	149	340	0.00000075699	123
286	0.00000083019	149	341	0.00000075576	123
287	0.00000082870	148	342	0.00000075453	123
288	0.00000082722	147	343	0.00000075330	122
289	0.00000082575	147	344	0.00000075208	122

T	$\frac{0.0012932}{760(1 + 0.00367T)}$	Diff.	T	$\frac{0.0012932}{760(1 + 0.00367T)}$	Diff.
345	0.00000075086	121	348	0.00000074723	120
346	0.00000074965	121	349	0.00000074603	120
347	0.00000074844	121	350	0.00000074483	

T-t	$1 + k(T-t)$	T-t	$1 + k(T-t)$	T-t	$1 + k(T-t)$	T-t	$1 + k(T-t)$
35	1.00096	115	1.00326	195	1.00581	275	1.00841
40	1.00110	120	1.00340	200	1.00596	280	1.00856
45	1.00124	125	1.00355	205	1.00610	285	1.00892
50	1.00138	130	1.00369	210	1.00625	290	1.00907
55	1.00151	135	1.00392	215	1.00640	295	1.00923
60	1.00165	140	1.00407	220	1.00655	300	1.00939
65	1.00179	145	1.00421	225	1.00670	305	1.00954
70	1.00193	150	1.00436	230	1.00685	310	1.00970
75	1.00207	155	1.00451	235	1.00719	315	1.00985
80	1.00220	160	1.00465	240	1.00734	320	1.01001
85	1.00241	165	1.00480	245	1.00749	325	1.01017
90	1.00255	170	1.00494	250	1.00765	330	1.01032
95	1.00269	175	1.00509	255	1.00780	335	1.01048
100	1.00284	180	1.00523	260	1.00795	340	1.01064
105	1.00298	185	1.00551	265	1.00810	345	1.01079
110	1.00312	190	1.00566	270	1.00826	350	1.01095

XI.—On the Composition, Value, and Utilization of Town Sewage.*

By J. B. LAWES, Esq., F.R.S., F.C.S., and J. H. GILBERT, Ph.D., F.R.S., F.C.S.

Position of the Sewage Question.

It is no less true than strange that, after so many centuries of advance in regard to almost every other requirement of civilised life, the lesson should not yet have been learnt of how to dispose of the excretal matters of large populations, in such a manner as to secure both their collection and removal without nuisance and injury to

* The substance of this paper was given as a discourse before the Chemical Society, February 1, 1866, by Dr. Gilbert.

health, and their economical utilization for the reproduction of food. But it is undoubtedly the fact that, hitherto, where utilization has been the most complete, comfort and health have generally been in the greatest degree sacrificed, and where, on the other hand, the refuse matters of town populations have been the most rapidly and perfectly removed from their dwellings, there has been either no utilization at all, or it has been most imperfectly attained.

Sewage, the foul stream which flows through the underground veins and arteries of our great cities, carrying with it the excretal and other refuse matters of large populations, hitherto to little better purpose than to be wasted, and to be a source of pollution to our rivers—to destroy their fish, injure their channels, and render them unfit as a water-supply to other towns—is the product of the, to us, modern, but in the history of the world only resuscitated and elaborated, water-system of town purification. There is no doubt that excretal and other refuse matters are removed from habitations more rapidly, with less nuisance to the occupants, and with less injury to their health, by means of water, than in any other way hitherto practised on a large scale. But such is the dilemma into which the progress of modern civilisation in this direction has brought us in this country, so far as utilization and the condition of our rivers are concerned, that some authorities, especially on the Continent, incline to the reactionary conclusion that a return to the cesspool system, or rather the adoption of some improved barrel, tank, or cesspool system, of collection and removal without admixture with extraneous water, is inevitable.

Before, therefore, entering upon the question of the composition, value, and modes and results of the utilization of dilute town sewage, it will be well to call attention, though very briefly, to some of the results of experience hitherto attained, under other systems of town purification, and other modes of utilization of the products, than the modern ones by means of water.

China and Japan are frequently cited as affording examples of very perfect utilization of human excretal matters, and, as a consequence, of great productiveness of the soil and great concentration of population on a given area of land. The manner of collecting, removing, and transporting human excretal matters in those countries is, however, such as to be quite inadmissible with our modern notions of cleanliness, decency, comfort, and health.

It is frequently stated that in Belgium human excretal matters are very perfectly utilized, and realise considerable money return

to the town populations. Indeed, in one of the applications made only last year to the Metropolitan Board of Works for the concession of the Southern sewage of the Metropolis, and still under the consideration of that body, it is stated that the excretal matters sell in Belgium for something over £1 per person per annum.

There is no doubt that in some parts of Belgium the solid, and a portion of the fluid excrements of the town populations are collected, as free as possible from extraneous water, in receptacles of more or less perfect construction, and periodically removed for application to the land, and that the land so fertilised is very productive. From observation and inquiry made in some of the towns in question, it may, however, be safely affirmed, that the practices adopted are attended with, at any rate, so much of nuisance and discomfort as would not now be permitted in this country; whilst it would appear that a considerable proportion of the urine of the populations escapes collection and utilization. As the result of the same inquiries, it was concluded that, in no case, did the town population realise by the disposal of their excretal matters as much as averaged one franc per head per annum.

The conclusion that, as a rule but little, and frequently nothing, is realised by town populations when their excretal matters are collected under more or less modified cesspool or tank systems, as free as possible from extraneous water, and so removed for application to the land, is fully confirmed by the results of an inquiry conducted by a Commission sent out by the Prussian Government in 1864, to investigate the modes of collection, removal, and utilization, in various localities, with a view to the adoption of improved plans for the city of Berlin.

The Prussian Commissioners, Herren C. v. Salviati, O. Röder, and Dr. Eichhorn, visited and reported upon, not only the Belgium towns of Ghent, Ostend, and Antwerp, but likewise Hanover, Cologne, Metz, Carlsruhe, Strasburg, Basle, Lyons, Zurich, Munich, Nuremberg, Dresden, and Leipzig; and their report shows not only that the householders seldom realised anything like a franc per head per annum for their excretal matters, but that in the majority of cases it cost them something for the removal. Nevertheless, looking to the position and local circumstances of Berlin, and especially to the results of the water-system in this country hitherto, the Commissioners deprecate the adoption of that system for that city, and recommend more perfect arrangements and more stringent regulations for the emptying

and removal of the contents of existing cesspools, and, where practicable, the adoption of a system under which the excretal matters of each house are to be collected in a barrel placed at the bottom of the shaft leading from the closets, which, when removed, is covered with a closely fitting lid, and is of such dimensions that two men can carry it by means of handles attached for that purpose. They seem to anticipate little, if any, pecuniary profit to the town from these arrangements, but consider that they will be attended with scarcely any, or even no, nuisance or discomfort, and that by their means a large amount of valuable manure will be provided in a convenient form for transport and utilization. There can, however, we think, be little doubt that under such a system the collection and removal must be attended with considerable nuisance, that the greater part of the urine will be lost, and that the cost of the collection, removal, and transport will be such as to render the utilization unprofitable beyond a comparatively limited distance from the city.

There is little probability that the difficulties of the water-system will lead us in this country to have recourse again in our large towns to any system of cess-pools, tanks, or barrels, however improved; but it may be well here to notice one or two attempts that have been made within the last few years to obviate the use of water, and thereby to avoid the pollution of rivers, and to secure the collection of the manurial matters in a form more readily transportable by ordinary means, and, therefore, more applicable for general agricultural use: for there cannot be a doubt that if any system could be devised by which human excretal matters could be collected and removed from dwellings, without either nuisance or injury to health, and obtained economically in a concentrated, dry, and portable condition, their utilization would be much more perfectly attained by such means than is at all likely, or even possible, under the water-system.

Perhaps the most noticeable attempt of the kind in question is that which has been made at Hyde, in Lancashire, a manufacturing town of more than 20,000 inhabitants. Some few years ago a company contracted to carry out what they call the "Eureka system." They provided boxes to fit in at the back of the privy or closet of nearly every house, leaving scarcely a water-closet in the place. Some disinfecting or deodorising mixture is put into the box before it is placed in its position, and the box is exchanged for a fresh one after a certain number of days, according to the

number of individuals frequenting the place ; and it is stipulated that neither extraneous water, nor any other than human excretal matters, should be accumulated in these receptacles. The boxes, when removed, are covered with closely fitting lids, and so transported in closed vans to a manure manufactory close to the town. Here the matters are first well mixed, and then strained to remove rags, which are washed and sold for paper-making. More disinfectant is then added, and the matter concentrated by distillation, the distilled water being sold to dyers and bleachers. The residue thus thickened is then mixed with coal-ashes, which are collected in the houses in casks left for the purpose, and before being used are re-burnt in a reverberatory furnace, and finely ground.

On visiting Hyde in 1863, it certainly appeared that the mode of collection and preparation adopted was attended with, at any rate, very little unpleasant odour, and it was maintained by the advocates of the system, that its adoption had been successful in a sanitary point of view ; though even at that time some difference of opinion existed, and a controversy on the subject was in progress. The system is still in operation ; but we are informed that the feeling of the inhabitants is very strong against the maintenance of the works in the neighbourhood ; indeed, that an injunction against them has been sought, though unsuccessfully, and that proceedings by indictment are now being taken. This opposition has reference not to the mode of collection, but to the conducting of the manufacture so near to the town, But, whether or not, the plan of collection and removal may have proved successful, so far as the avoidance of nuisance and injury to health are concerned, the process of manufacture seems, unfortunately, to offer but little prospect of successful utilization, so far at least as can be judged from the results of an analysis made at Rothamsted, of a sample of the manure obtained direct from the works. It was found to contain only between 1 and 2 per cent. of ammonia. Such a manure, although it might be useful enough when applied in quantities of many tons to the acre, would obviously be not worth more than its carriage beyond the distance of a very few miles. Besides the great dilution of the more valuable manurial matters by the admixture with ashes, a little consideration of the habits of the people is sufficient to account for the small quantity of ammonia found in the manure ; for it is obvious that little of the urine beyond that passed once a day with the fæces would reach the

boxes, and so find its way into a manure thus collected and prepared.

One more dry system, the offspring of the difficulties of the wet one, should be briefly noticed, namely, that of the Rev. Mr. Moule. Mr. Moule has invented and patented an arrangement for the use of dry sifted earth, instead of water. He states that by the use of about 4lbs. per head per day of finely sifted clay, deposited by means of a mechanical arrangement upon the faecal matters as soon as passed, they are at once entirely deodorised, and in a few weeks are so entirely disintegrated that neither excretal matters nor paper can be detected in the mass, which, he says, looks and smells like fresh earth, and may, after resifting, be re-used, until it has done duty four times over, by which, of course, there is not only a great saving of material, but the value of the manure is considerably increased.

Very obvious objections to such a system are—the difficulties of the supply and preparation of the soil in the case of towns, or even in the country in wet seasons; the fact that but little of the urine, containing as it does so large a proportion of the valuable manurial constituents of human excretal matters, would reach the compost so prepared; and that, in the manure produced, the more valuable matters would be diluted with so large a proportion of comparatively useless material, that beyond a very short distance the cost of carriage would be all that the manure was worth. On the other hand, that the adoption of such a system would be a great improvement in a sanitary point of view, in the cases of sick rooms, detached houses, or even villages, where the water-system is not available, and that it might be even economical where the earth for preparation and absorption, and the land for utilization, are in close proximity, may, perhaps, be readily granted. But we are certainly not so sanguine as the Rev. Mr. Moule, who seems to think that with the aid of Earth-closet Companies, his plan is as practicable for large towns as is the supply of water, gas, and coal, at present, and much more so than the removal and utilization of dilute town sewage.

Whilst it must be admitted that the agricultural utilization of human excretal matters has, hitherto, been much more completely attained under the system of collection without water than under our new one with it, it must not be forgotten that neither on the continent of Europe nor in this country has such utilization resulted in any substantial profit to the towns; and that it is, with

the recorded results of China and Japan before us, and after so many centuries of experience nearer home, of at least comparatively successful utilization, that the old systems have been abandoned, as utterly inconsistent with advance in habits and notions of cleanliness, and with the maintenance of the comfort and health of large populations. Nor do the modifications of the dry systems, to which brief reference has been made, seem to hold out any hope of general and permanent applicability to large populations, looking, as we must, to the combined requirements of convenience, comfort, health, and utilization. Our water-system of house defecation and town cleansing is, on the other hand, scarcely more than a generation old. By its means excretal and other refuse matters are more rapidly removed from dwellings than is possible by any other; and, independently of the increased comfort and freedom from nuisance obvious to all, sanitary statistics have abundantly shown increased immunity from zymotic diseases, and increased longevity, as the result of the adoption of that system. True it is that these advantages have, hitherto, been attained at the cost of the almost universal sacrifice of the manure, and of great injury to our rivers.

This, then, is admittedly the existing dilemma of our modern practices. But public attention is now so thoroughly directed to the subject, that little fear need be entertained that either the systematic non-utilization of the sewage, or the pollution of our rivers by it, will long be permitted. Least of all is it reasonable to find discouragement in the fact, that the system which has done so much for some of our town populations in so short a time, should not, at this early stage of its trial, have accomplished all that might be desired, or to conclude that the nuisances and difficulties incident to the old plans, which have remained unremedied through so many centuries, have much better chance now than formerly of being successfully obviated.

Assuming that there is more likelihood of the general applicability, success, and permanence of the water, than of any other system of urban defecation, it becomes important to consider the composition, the value, and the modes and results of the utilization of the product of that system, namely, *dilute town sewage*.

Many plans have been proposed for the separation of the valuable constituents from sewer-water, and the manufacture of them into dry and easily portable manure. But whilst several of these plans have been successful in separating the whole of the insoluble

or sedimentary matter, and even some small portion of the soluble constituents, leaving the fluid to a great extent, or at any rate temporarily, purified, and in a much less objectionable condition for turning into rivers, none have succeeded in either adequate or permanent purification, or in the separation of the more valuable manurial matters, and the production of a concentrated solid sewage-manure, having a sufficient value to be remunerative, and to bear the cost of transport more than a very few miles;* nor when we consider the great solubility of some of the more active manurial constituents of sewage, and the great dilution of them in the sewage, can any hope be held out of so desirable a consummation;—desirable, indeed, for if human excretal matters, the residue of the constituents consumed as food, cannot be recovered in the form of a concentrated, dry, and easily transportable manure, little hope can be entertained of their re-distribution over anything like the area from which they came, or of their general use for the direct reproduction of the varied descriptions of food which were their source.

The questions arise: What is the amount, and what approximately the money value for the purposes of manure, of the constituents contributed to sewage by a given population? What their state of dilution in sewer-water? To what soils and crops is dilute sewage the most applicable? What is the money-value realisable in practice by sewage utilization? What are the conditions of profit or loss to towns of such utilization?

Composition and Value of Town Sewage.

It is one thing to determine the amount of constituents contained in sewage, or contributed to it by a given population, and to estimate their value accordingly, as if they existed in the dry and portable condition of the various concentrated manures of known value in the market; but it is obviously quite another to settle the really available or realisable value of the same consti-

* For information in regard to some of the plans proposed for the partial purification of sewage-water, or for the separation of a solid manure from it, see—"On the Application of Sewage to Agriculture," by Dugald Campbell, Esq., F.C.S., Chem. Soc. Qu. J. vol. x. p. 272. "Report of Chemical Investigations relating to Metropolitan Main Drainage Question," by A. W. Hofmann, LL.D., F.R.S., and Henry M. Witt, F.C.S., Report on Metropolitan Drainage, 1857. Deodorization of Sewage, Second Report of the Royal Sewage Commission, 1862., Appendix No. 6, p. 64.

trients when they are distributed through an enormous volume of water, and if they must be transported and utilized in that condition. Let us first consider what may be called the theoretical value of the constituents of sewage, or their estimated value, taking as the measure the value of the same constituents in dry and portable manures.

Numerous authorities have undertaken the consideration of this question, and two chief methods have been adopted. One of these has been to take samples of sewage and determine its composition by analysis, to adopt such estimates as are at command relating to the amount of sewage available within a given time or from a given population, and so to reckon the amount and value of the constituents in a given quantity of sewage, or per head, or for a given number of persons, per annum. Another is to base the calculation upon the amounts of feces and urine, or of the various constituents of these, which have been recorded as voided by individuals of different sexes and ages—sometimes making allowance, and sometimes not doing so, for other than human excretal matters reaching the sewers.

First, as to the results attained when the calculation is based upon the analysis of sewage, and estimates of the amount of it yielded by a given population.

In estimates of the value of the constituents of sewage, about three-fourths of the total value has generally been attributed to the ammonia (or nitrogen reckoned as ammonia); and it so happens that if a value of 8d. be put upon every lb. of ammonia shown by analysis to be contained in sewage, or if for each grain of ammonia per gallon, a value of one farthing be given to the total constituents in 1 ton of the sewage, the result will, in either case, agree almost exactly with that obtained by the elaborate method of giving the currently adopted market values to the several constituents, taking dry and portable manures as the standard.

One or two illustrations may be given of the applicability of the latter mode of reckoning. In the summer of 1863, Baron Liebig, adopting as the basis of his calculations an analysis of the Dorset Square sewage by Mr. Way, which showed nearly 18 grains of ammonia per gallon, estimated that (provided the quantity of phosphates which he considered requisite to render the whole of the ammonia available were employed with the sewage) the constituents in 1 ton of sewage of that composition would be worth

about 4d. Now, according to our mode of estimate stated above, 18 grains of ammonia per gallon would indicate a value of 18 farthings, or $4\frac{1}{2}$ d., for the total constituents in 1 ton of the sewage. In January, 1865, Baron Liebig assumed the average sewage of the Metropolis to contain only 7·2 (instead of 18) grains of ammonia per gallon; and he estimated the value of the constituents in 1 ton of such sewage to be rather over $1\frac{3}{4}$ d. Our estimate would also give rather over 7 farthings, or $1\frac{3}{4}$ d. Lastly on this point, in 1857, Messrs. Hofmann and Witt concluded from their investigations that the average *dry weather* sewage of the Metropolis contained about 8·2 grains of ammonia per gallon; and calculating the value of the sewage according to the amount of ammonia, organic matter, phosphoric acid, and potassa, they estimated that of the total constituents in 1 ton of such sewage to be about 2·11d. It is clear that giving a value of $\frac{1}{4}$ d. to the total constituents per ton of sewage, for each grain of ammonia per gallon, would yield almost identically the same result.

It is obvious, therefore, that in this part of the discussion we may, for all practical purposes, safely disregard everything but the amount of ammonia contained in the sewage, and that by so doing the consideration of the subject will be greatly simplified. It will be seen, too, that in adopting this course we do not in any way ignore, or undervalue, the importance of the associated constituents, but, on the contrary, accord to them the same value as Baron Liebig, Messrs. Hofmann and Witt, and others, have done by a much more elaborate process of calculation.

Numerous analyses have been made from time to time of samples of the Metropolitan and other sewage; and sometimes very important theoretical conclusions, and even propositions for the investment of enormous amounts of capital in utilization schemes, and anticipations of enormous profits from their adoption, have been based upon the results of a single analysis. Such, however, is the variation in the dilution of the sewage of any one locality at different times, that it is quite impossible to draw any safe conclusions from the results of analysis without carefully taking into consideration the circumstances affecting the dilution at the time of sampling. This is strikingly illustrated by the results given in Table I., in which are recorded the grains of ammonia per gallon, as determined by various experimenters, in samples of the Metropolitan sewage, taken at different times and places, and also the estimated value of the total constituents in one ton of the sewage,

reckoned according to the number of grains of ammonia per gallon as above referred to.

TABLE I.

Grains of Ammonia per gallon in different samples of Metropolitan Sewage, and estimated value of Constituents in one ton.

Authority.	Name of Sewer.	Time of Sampling.	Ammonia per Gallon.	Estimated Value per ton.
			Grains.	d.
Way.....	Barrett's Court	Day	41·28	10 $\frac{1}{4}$
	Dorset Square	Day	17·96	4 $\frac{1}{2}$
Letheby	The Fleet	Noon	5·15	1 $\frac{1}{4}$
		Midnight	8·50	2
	London Bridge	Noon	6·69	1 $\frac{3}{4}$
		Midnight	8·10	2
	Dowgate Dock	Noon	10·03	2 $\frac{1}{2}$
		Midnight	3·43	0 $\frac{3}{4}$
	Iron Gate	Noon	8·13	2
		Midnight	6·20	1 $\frac{1}{2}$
	Paul's Wharf	Noon	12·01	3
		Midnight	3·13	0 $\frac{3}{4}$
	Whitefriar's Dock	Noon	5·35	1 $\frac{1}{4}$
		Midnight	3·41	0 $\frac{3}{4}$
	Custom House, West ..	Noon	6·25	1 $\frac{1}{2}$
		Midnight	8·17	2
	Custom House, East....	Noon	7·28	1 $\frac{3}{4}$
		Midnight	15·01	3 $\frac{3}{4}$
Hofmann & Witt ..	Hambro' Wharf	Noon	7·69	2
		Midnight	5·69	1 $\frac{1}{2}$
	Wool Quay	Noon	6·95	1 $\frac{3}{4}$
		Midnight	5·00	1 $\frac{1}{4}$
	Tower Dock	Noon	10·02	2 $\frac{1}{2}$
		Midnight	7·15	1 $\frac{3}{4}$
	Mean	7·24	1 $\frac{3}{4}$
	Savoy Street	24 hours	8·21	2 $\frac{1}{10}$

The results given at the head of the table, on the authority of Mr. Way, are those of probably the first analyses made of the Metropolitan sewage, and it is only fair to say that at the time he published them, he expressly stated that although they showed that there was great manurial value in sewage, yet they could not be taken as in any way affording a measure of that value. It was, however, upon the analysis of the sample of the Dorset Square sewage, showing nearly 18 grains of ammonia per gallon, that Baron Liebig based his calculations as to the value of the Metropolitan

sewage in 1863 ; and the advocates of particular sewage schemes, and even members of Parliamentary Committees, have sought to found much upon the results of those analyses.

From the varying circumstances under which the samples analysed by Dr. Letheby were taken, as indicated in the table, it is obvious that the results, though very valuable in that respect, must be considered rather as illustrations of the variation in composition of the Metropolitan sewage at different times and places, and as showing the danger of founding important practical conclusions upon the results of the analysis of an individual sample, than as affording direct evidence as to the average composition of the Metropolitan sewage.

The sample analysed by Messrs. Hofmann and Witt was a mixture of equal portions taken every hour during twenty-four hours of dry weather, and there is no doubt that that sample had better claims to be taken as representing the average dry weather sewage of the Metropolis than any other that had up to that time been collected and examined. It was upon the analysis of this sample that Messrs. Hofmann and Witt, calculating the value of the ammonia, organic matter, phosphoric acid, and potassa, which it contained, estimated that the constituents in one ton of such dry weather sewage would be worth rather over 2d., and, according to the information supplied to them for the purpose of their calculations, the quantity of sewage, exclusive of rainfall, would be about 158,000,000 tons per annum, or scarcely three-fifths as much as that assumed in the estimates of Baron Liebig and Mr. Thomas Ellis, as the total sewage, namely, 266,000,000 tons. Yet, Messrs. Hofmann and Witt's estimate of a little over 2d. for the value of the constituents in one ton of the normal dry weather sewage was taken by Mr. Ellis, in his application for the concession of the Metropolitan sewage, as applying to the whole amount of dilute sewage (inclusive of rainfall and subsoil water), which he estimated would be available for utilization (266,000,000 tons), and his calculations of profit to his Company and to the ratepayers were based upon this erroneous assumption.

To conclude in reference to the results recorded in Table I., attention may be called to the fact that the different samples show a variation of from about 3 to more than 41 grains of ammonia per gallon, representing approximately a difference of from about $\frac{3}{4}$ d. to about 10 $\frac{1}{4}$ d. for the estimated value of the total constituents in one ton of the sewage.

That the results of an analysis of a sample of sewage of any locality taken without careful reference to the circumstances of its dilution, are not only entirely inadequate as the basis of general conclusions, but may even be utterly misleading, is even more strikingly illustrated by the results next to be considered, which were obtained in the course of an investigation undertaken by the late Royal Sewage Commission.

Three members of the Commission, the late Mr. Henry Austin, C.E., Mr. Way, and one of the authors (J. B. Lawes) were appointed a sub-committee to undertake an investigation on the utilization of sewage. The agricultural experiments were conducted at Rugby, and their management, and the selection, collection, and preparation of samples for analysis, devolved upon the authors, the analyses being made in the laboratory of Mr. Way. The inquiry extended over a period of between three and four years, and involved the application of different quantities of sewage to meadow-grass and some other crops; the determination of the amounts of produce obtained; the feeding of fattening oxen and milking cows on the unsewaged and the sewaged grass; and the sampling, and more or less complete analysis, of the soil, of the sewage, of the drainage-water from the irrigated land, of the unsewaged and the sewaged grass, of the milk yielded by the cows fed upon it, &c., &c. It is proposed to embody in the sequel a brief abstract statement of some of the more important facts and conclusions brought out by the experimental inquiry above referred to, and the reader is referred for all fuller details to the Reports of the Commission.*

The mode of collecting samples of the Rugby sewage for analysis was, to take about a quart (from a gauge-tank holding between 3 and 4 tons, through which the sewage flowed before passing on to the land), at intervals of about two hours for several days together, well mix the quantity so accumulated, and take a sample of the mixture for analysis. 93 such mixed samples were collected and analysed, the period of collection extending over 31 months, from April, 1861, to October, 1863, inclusive. Table II. shows the highest, the lowest, and the average amounts of ammonia and total solid matter which the analyses of these numerous mixed samples indicated.

* Second and Third Reports of the Commission appointed to inquire into the best mode of Distributing the Sewage of Towns, and applying it to beneficial and profitable uses. 1862 and 1865.

TABLE II.

Showing the highest, lowest, and average amounts of Ammonia, and total Solid Matter, in mixed samples of Rugby Sewage at different times.

		Ammonia.		Total Solid Matter.	
		Grains per Gallon.	lbs. per 1000 Tons.	Grains per Gallon.	lbs. per 1000 Tons.
1861	Highest.....	15·64	500·5	216·5	6928
	Lowest	2·99	95·7	37·6	1203
	Mean of 24 analyses	6·39	204·5	75·1	2405
1861-2	Highest.....	11·38	364·2	129·3	4138
	Lowest	2·55	81·6	50·5	1616
	Mean of 34 analyses	5·95	190·4	80·3	2570
1862-3	Highest.....	12·81	409·9	269·9	8637
	Lowest	3·14	100·5	62·2	1989
	Mean of 35 analyses	7·08	226·5	103·2	3302

Thus, although each sample analysed was a mixture of samples taken over several days together, as above described, there was a variation among the 93 samples of from $2\frac{1}{2}$ to $15\frac{1}{2}$ grains of ammonia, and from $37\frac{1}{2}$ to 270 grains of total solid matter, per gallon; or, of from $81\frac{1}{2}$ to $500\frac{1}{2}$ lbs. of ammonia, and from 1203 to 8,637 lbs. of total solid matter, per 1,000 tons of sewage. Reckoned according to the number of grains of ammonia per gallon, the estimated value of the total constituents in 1 ton of sewage varied from about $\frac{5}{8}$ d. to nearly 4d.

Notwithstanding the very great differences in the composition of the Rugby sewage at different times, much greater, indeed, than could have been expected, considering the circumstances of the sampling, it is still believed that the mean of so many determinations may be taken as indicating, at any rate approximately, the average composition of the Rugby sewage over the period to which they refer. The probability of this will be seen on a consideration of the average results for each of the three seasons, and for the total period of 31 months of collection, given in Table III.

TABLE III.

Mean Composition of Rugby Sewage, in 1861, 1862, and 1863.

Constituents		Means of			
		24 Samples, April to Oct. 1861.	34 Samples, Nov. 1861 to Oct. 1862.	35 Samples, Nov. 1862 to Oct. 1863.	93 Samples, April 1861 to Oct. 1863.
Grains per gallon.					
In suspension	Inorganic	14·36	20·86	34·45	24·30
	Organic.....	14·16	16·84	24·03	18·85
	Total	28·52	37·70	58·48	43·15
In solution	Inorganic	36·34	34·42	36·80	35·81
	Organic.....	10·28	8·20	7·92	8·63
	Total	46·62	42·62	44·72	44·44
Total inorganic....		50·70	55·28	71·25	60·11
Total organic		24·44	25·04	31·95	27·48
Total solid matter..		75·14	80·32	103·20	87·59
Ammonia	In suspension	1·41	1·47	1·86	1·60
	In solution	4·98	4·48	5·22	4·89
	Total	6·39	5·95	7·08	6·49
lbs. per 1000 tons.					
In suspension	Inorganic	460	668	1102	773
	Organic.....	453	539	769	603
	Total	913	1207	1871	1381
In solution	Inorganic	1163	1101	1178	1146
	Organic.....	329	262	253	276
	Total	1492	1363	1431	1422
Total inorganic....		1623	1769	2280	1924
Total organic		782	801	1022	879
Total solid matter..		2405	2570	3302	2803
Ammonia	In suspension	45	47	60	51
	In solution	159	143	167	157
	Total	204	190	227	208

It is seen that the mean result of the analyses of 24 samples collected from April to October, inclusive, 1861, indicates 6.39 grains of ammonia per gallon; that of 34 samples collected from November 1861, to October 1862, inclusive, 5.95 grains, and that of 35 samples, collected from November 1862, to October 1863, inclusive, 7.08 grains. This difference in the average concentration of the sewage of the different seasons is perfectly consistent with the difference in the character of the seasons themselves. Thus, the season of 1861-2 was much the wettest, and its sewage was, accordingly, the most dilute; the season of 1862-3 was much the driest, indeed extremely dry, and its sewage was the strongest; and the season of 1861 being intermediate in this respect, its sewage was of intermediate strength.

Looking to the average result of the 93 analyses, it will be observed that the sewage contained about $87\frac{1}{2}$ grains per gallon of total solid matter, of which about two-thirds was inorganic, and one-third organic. About half of the total solid matter was in suspension, and half in solution: of the half in suspension about four-sevenths was inorganic and three-sevenths organic, and of the half in solution, about four-fifths inorganic, and one-fifth organic. Lastly, of the nitrogen reckoned as ammonia, about one-fourth was in suspension, and three-fourths in solution.

The mean of the 93 analyses shows about $6\frac{1}{2}$ grains of ammonia per gallon, indicating a value of about $1\frac{1}{3}$ d for the total constituents in 1 ton of the sewage. But taking into consideration the fact that the samples were not collected at exactly equal intervals throughout the total period, it is concluded that, by taking the mean result for each of the 31 months separately, and then the mean of the 31 means so obtained, the result will more nearly represent the real average composition of the sewage of the whole period, than will the direct mean of the 93 analyses; and the calculated average so obtained indicates about 7, instead of only $6\frac{1}{2}$, grains of ammonia per gallon.

From all the information at command as to the population contributing to the sewers, the water-supply, the rainfall, and the drainage area, it was concluded that, taking the average of seasons, there are about 60 tons of sewage per head of the population of Rugby, per annum; but that, as the period of the experiments was drier than usual, the amount probably then reached to only about 55 or 56 tons.

Now, if we reckon $6\frac{1}{2}$ grains of ammonia per gallon, and 60

tons of sewage per head per annum, it would result that $12\frac{1}{2}$ lbs. of ammonia were contributed annually for each average individual of the mixed population, of both sexes and all ages; or, if we reckon 7 grains of ammonia per gallon, and 56 tons of sewage per head per annum, we equally arrive at the amount of $12\frac{1}{2}$ lbs. of ammonia per head per annum; and from a careful consideration of the Rugby results, it was concluded, at the time the Report was issued, that this probably very nearly represented the actual truth.

Having, then, by means of the results of a great many analyses of sewage, and a consideration of the amount of sewage contributed by each average individual of the population, estimated that for each such average individual there would be about $12\frac{1}{2}$ lbs. of ammonia contributed to the sewer-water, let us next see what

TABLE IV.

Amount of Nitrogen reckoned as Ammonia, and estimated value of total Constituents, in Human Voidings, per head per annum.

	Ammonia.	Value of Total Constituents.
Adult Males; Hofmann and Witt.		
Urine	lbs. 15·8	s. d. 10 0 $\frac{1}{2}$
Fæces	2·3	1 8 $\frac{3}{4}$
Total	18·1	11 9 $\frac{1}{4}$
Adult Males; Thudichum.		
Urine	15·9	10 3 $\frac{1}{2}$
Average, both sexes and all ages; Hofmann, Witt, and Thudichum.		
Urine	11·32	7 3
Fæces	1·64	1 2 $\frac{3}{4}$
Total	12·96	8 5 $\frac{3}{4}$
Average, both sexes and all ages; Lawes and Gilbert.		
According to { Food.....	12·2	} 8 4
{ Voidings....	12·6	
{ Voidings....	12·7	
Mean	12·5	

result is arrived at by the other method of computation which has been referred to, namely, by the calculation of the amounts of fæces and urine, or of the various constituents of these, recorded as voided by persons of different sexes and ages. Table IV. very concisely summarises the information available on this subject, so far as it is necessary for our present purpose.

To check their estimates founded on the analysis of the 24-hours' mixed sample of the Savoy Street sewage, Messrs. Hofmann and Witt took the amount of urine estimated to be daily voided by an adult, and the amount of fæces recorded as voided on the average per head of the body-guard of the Grand Duke of Hesse Darmstadt (but allowing, as they said, a little more for "John Bull"), and applying the results of Berzelius' analysis of urine, and those of the analyses of Way, Liebig, and Wesarg, of fæces, they calculated the amount of ammonia, and other constituents, daily voided by such persons. According to their data, the amount of ammonia annually voided by an adult male was, in urine 15·8, in fæces 2·3, total 18·1 lbs.; and the estimated money value of the constituents was in urine 10s. 0½d., in fæces 1s. 8¾d., total 11s. 9½d. The result so obtained for adult males they take as applicable to each individual of a mixed population, of both sexes and all ages, assuming that other matters reaching the sewers would probably make up the difference. There can be little doubt that this was making far too liberal an allowance for other than human excretal matters contributing to the value of the sewage.

Some years later, in 1863, Dr. Thudichum, from much more comprehensive data, gave for the urine alone of an adult male 15·9 lbs. of ammonia, and 10s. 3½d. of value; amounts which, it will be seen, are almost identical with those of Messrs. Hofmann and Witt.

But Dr. Thudichum, instead of directly applying the results obtained for an adult male to each average individual of a mixed population, considered that two adult males would approximately represent 2·8 such average persons. Now, if we take the mean of the estimates of Messrs. Hofmann and Witt, and Dr. Thudichum, with regard to the urine, and those of Messrs. Hofmann and Witt with regard to the fæces, of an adult male, and reduce both in the proportion of from 2·8 to 2, according to Dr. Thudichum's basis of calculation, we shall, provided the estimates of these authorities be correct, arrive at amounts approximately applicable to an average individual of a mixed population of both

sexes and all ages. By this process, as the Table shows, we have nearly 13 lbs. of ammonia, and nearly 8s. 6d. of value, to represent the mixed voidings of such an average individual.

In 1854, the authors, basing their estimates on very comprehensive data, relating both to the amounts of constituents consumed in the food, and voided in the urine and fæces, of persons of different ages and both sexes, concluded that probably about 10 lbs. of ammonia, and total constituents of the estimated manurial value of about 6s. 8d., were annually contributed to sewage per individual of a mixed town population. More recently, for the purposes of the Report of the Royal Sewage Commission, all the estimates relating to the constituents voided were carefully revised, bringing into the calculations such further information as was then at command;* and the results so obtained are recorded in the Table (IV).

The amount of nitrogen estimated to be annually consumed in the food of an average individual was deduced from the calculation of 86 dietaries, arranged in 15 classes, according to sex, age, activity of mode of life, and other circumstances, and corresponded to about 12·2 lbs. of ammonia; from which, of course, a deduction has to be made for the nitrogen retained in the body, and for loss in various ways. When the calculation was based upon determinations or computations of the amounts of nitrogen or ammonia-yielding matters voided by persons of different sexes and ages, the result arrived at was 12·6 lbs. of ammonia; and when upon the recorded amounts of fresh urine and fæces voided, and the average composition of these, the amount indicated was 12·7 lbs. of ammonia per head per annum. A careful consideration, however, of the circumstances of the majority of the cases contributing to the averages among those divisions of the population in relation to which the evidence is the most plentiful, and of the relative character of the results where it is the most deficient, led to the conclusion that the estimate of 12·6, or 12·7 lbs. for the amount

* For nearly the whole, if not the whole, of the data upon which the new estimates are based, see "On the Sewage of London," by J. B. Lawes, F.R.S., *Journal of the Society of Arts*, March 9, 1855; "The Composition of the Urine in Health and Disease," by E. A. Parkes, M.D., 1860; "On an Improved Mode of collecting Excrementitious Matter, with a view to its Application to the benefit of Agriculture, &c.," by J. L. W. Thudichum, M.D., F.C.S., *Journal of the Society of Arts*, May 15, 1863; and "On the Elimination of Urea and Urinary Water, in relation to the period of the Day, Season, Exertion, Food, &c., &c.," by Edward Smith, M.D., LL.B., F.R.S., *Philosophical Transactions*, vol. cli, p. 747.

of ammonia voided annually by an average individual of a mixed population, was in all probability too high.

Reviewing the whole of the evidence, both that relating to the composition and the amount of the Rugby sewage, and that relating to the amount of constituents voided by an average individual, it was concluded that the amount of ammonia annually contributed to the sewer-water by an average person of a mixed population was pretty certainly more than 10 lbs., as formerly assumed, but probably less than 12 lbs.; and, making allowance for the fractional part of the excretal matters of horses, cows, dogs, and other animals, of the refuse of slaughter-houses, of soot, and of other refuse matters that may reach the sewers, it was concluded that still not more than $12\frac{1}{2}$ lbs. of ammonia would be contributed annually to the sewers from all sources, per head of mixed town population. This would indicate an estimated value of 8s. 4d. per annum for the total constituents in the sewage for each average individual.

It was admitted, however, to be a great desideratum, that when the Main Drainage of the Metropolis came to be completed, and the works to be in full operation, competent persons should be appointed to superintend the gauging, sampling, and analysis of the sewage, with a view to providing data which might serve to determine satisfactorily and conclusively the approximate amount, and average composition, of the Metropolitan sewage, as it will have to be dealt with in any plan of utilization, and also the relation of population to the composition of sewage generally.

Since the publication of the Report of the Commission, in March 1865, numerous gaugings and samplings of the sewage of the mid- and high-level sewers North of the Thames have been undertaken, and many samples have been analysed by Mr. Way. The results of this inquiry have not yet been published; but from information kindly communicated by Mr. Way, we are enabled to state their general bearing, so far, upon the point now under consideration.

From these new results it appears very probable that the amount of dry weather sewage averages only about two thirds as much per head of the population as that generally supposed before, and assumed both in the inquiries of Messrs. Hofmann and Witt, and in the Report of the Sewage Commission; but the average amount of ammonia per gallon now found by Mr. Way in the dry weather sewage very nearly approaches that arrived at by Messrs. Hofmann and Witt. Both Mr. Way and Mr. Cresy

frankly admit, however, in accordance with common experience the further a subject is investigated, that there are still many open questions, the settlement of which may materially affect the proper interpretation of the new gaugings.

Assuming them to indicate the result at present supposed, and above stated, it follows that the total amount of ammonia yielded by a given population will be only about two-thirds as much as that estimated by Messrs. Hofmann and Witt, on applying the results of their analysis to the higher estimated amount of the dry weather sewage. It further follows, from the same evidence, that the amount of ammonia annually contributed to the sewage, from all sources, per head of a mixed population, is more nearly 10 lbs., as formerly concluded by the authors, than $12\frac{1}{2}$ lbs., as more recently estimated; and if this result should be confirmed, their former estimate of 6s. 8d. will more nearly represent the calculated annual value of the total constituents yielded per head of the population than the more recent one of 8s. 4d. It would then have to be concluded, as indeed is not improbably the case, that, in the calculations based on the mean composition and the estimated total amount of the Rugby sewage, the latter had been taken at too high a figure, too large a proportion of the rainfall having been assumed to reach the sewers; and that, in the estimates founded on the recorded amounts of constituents voided, the incompleteness of the records, as already pointed out, had, as was supposed, led to too high an estimate.

We have, then, from 10 to $12\frac{1}{2}$ lbs. of ammonia, and an estimated value of from 6s. 8d. to 8s. 4d. for the total manurial constituents, contributed to sewage by each average individual of a mixed town population. Adopting these amounts, the questions arise—What will be the amount of ammonia, and what the estimated value of the constituents, in a given amount of sewage, at different dilutions? These points are illustrated in Table V.

TABLE V.

Ammonia, per gallon, and estimated value of total Constituents in one ton, of Sewage at different dilutions.

Dilutions supposed.		If 12½ lbs. Ammonia, per head per annum, from all sources.		If 10 lbs. Ammonia, per head per annum, from all sources.	
Per head per annum.	Per head per day.	Ammonia per gallon.	Estimated value per ton.	Ammonia per gallon.	Estimated value per ton.
Tons.	Gallons.	Grains.	Pence.	Grains.	Pence.
40	24½	9·77	2·44	7·81	2·00
50	30¾	7·81	1·95	6·25	1·60
60	36¾	6·51	1·67	5·21	1·33
70	43	5·58	1·43	4·46	1·14
80	49	4·88	1·25	3·91	1·00
90	55½	4·34	1·11	3·47	0·89
100	61½	3·91	1·00	3·13	0·80
200	122¾	1·95	0·50	1·56	0·40

According to the information supplied to Messrs. Hofmann and Witt, the dry weather sewage of the Metropolis amounted to between 36 and 37 gallons per head per day = about 60 tons per head per annum. Their analysis showed 8·2 grains of ammonia per gallon, equivalent to about 15¾ lbs. of ammonia per head per annum; and they reckoned the total constituents in 1 ton of such sewage to be worth 2·11d. But Table V shows that with a dilution of 60 tons, and with 12½ lbs. of ammonia per head per annum, there would be only 6·5 grains of ammonia per gallon, and total constituents in 1 ton of sewage worth only 1¾d.; and that with only 10 lbs. of ammonia per head per annum, there would be only 5·2 grains per gallon, and constituents worth only 1½d. in 1 ton of the sewage.

If, however, we take the dry weather sewage as indicated by the recent gaugings as more nearly 24 gallons per head per day = a rate of 40 tons per head per annum, we have then, with 12½ lbs. of ammonia per head per annum, 9·77 grains per gallon, and 2·44d. worth of constituents per ton; or, taking 10 lbs. of ammonia per head per annum, we have 7·8 grains per gallon, and constituents in 1 ton of an estimated value of nearly 2d. Now, Mr. Way's conclusion is, that the mid- and high-level dry weather sewage North of the Thames averages scarcely, but nearly, 8 grains of

ammonia per gallon, or almost exactly the amount last mentioned; and as Messrs. Hofmann and Witt's analysis shows 8·2 grains, it will be seen that both estimates, taken in connexion with the amended one as to the daily amount per head of the dry weather sewage, go to confirm the assumption that the amount of ammonia contributed to the sewage from all sources is much more nearly 10 than $12\frac{1}{2}$ lbs. per head per annum.

Whatever may eventually prove to be the average dilution of the dry weather Metropolitan sewage, the actual amount of fluid varies immensely from time to time, according to rainfall and other circumstances. When it exceeds a certain amount, as in the case of continuous rains or storms, a portion will pass at once into the Thames; and according to Mr. Bazalgette's figures it appears that this will happen when the volume is such as, if continuous, would represent something over 200 tons of fluid per head per annum. But, so far as information at present at command enables us to judge, it is probable that the amount, inclusive of rainfall and subsoil water, that will be available for utilization, will be somewhere about 80, and will pretty certainly not exceed 100 tons per head per annum; that is, about twice, or not more than twice and a half, as much as the most recently estimated dry weather flow. Of course, to result in anything like such averages, the dilution would sometimes be at a rate very much greater than those amounts would indicate. But it may be observed, by way of illustration, that with $12\frac{1}{2}$ lbs. of ammonia per head per annum, and an average of 80 tons of sewage, it would average less than 5 grains of ammonia per gallon, and only 1·25d. worth of constituents in 1 ton; or, reckoning an average dilution of 100 tons, it would average less than 4 grains of ammonia per gallon, and only 1d. of value of constituents in 1 ton. In like manner, reckoning only 10 lbs. of ammonia per head per annum, a dilution of 80 tons would show less than 4 grains, and of 100 tons little over 3 grains of ammonia per gallon, and an amount of constituents in 1 ton worth only 1d. and 0·8d. respectively.

In comparison with the figures just given, it may be stated that both Baron Liebig, and Mr. Thomas Ellis (one of the applicants for the concession of the Metropolitan sewage) assume its total amount at 266,000,000 tons per annum, which, with 3,000,000 population, represents nearly 90 tons per head per annum, and with this dilution the former estimates the sewage

to contain an average of 7.2, and the latter 8.2 grains of ammonia per gallon; the latter, as already stated, applying the estimate of Messrs. Hofmann and Witt for the dry weather sewage to the total estimated amount of available sewage, inclusive of rainfall.

It is sufficiently obvious that, however variable, the dilution of the constituents in town sewage is at any rate very great, and that in any scheme for the utilization of sewage large quantities will have to be dealt with. It will be useful, therefore, by way of illustration, and as a means of conveying a more definite idea of the extent of this dilution, to show the relation of a given amount—say 1,000 tons—of sewage of certain assumed dilutions, both to population, and to some well-known portable manure, such as Peruvian guano. This is done in Table VI, which shows the amount of guano which would supply as much nitrogen reckoned as ammonia as 1,000 tons of sewage of different dilutions, also the number of tons of sewage which would be equal in this respect to 1 ton of guano, and both on the alternative assumptions of $12\frac{1}{2}$ lbs., and 10 lbs., of ammonia per head per annum. The assumed dilutions are 40, 50, and 60 tons per head per annum, which may be taken to cover the minimum and maximum estimated rates of flow for the dry weather sewage of the Metropolis; 80 and 100 tons, which may be taken to represent the range for the average total available sewage, inclusive of rainfall and subsoil water, and 200 tons, the probable frequent dilution in wet weather.

TABLE VI.

Relation of Sewage to Peruvian Guano in amount of Nitrogen reckoned as Ammonia.

If Sewage per head per annum.	Contributing 1,000 tons Sewage.	If $12\frac{1}{2}$ lbs. Ammonia, per head per annum, from all sources.		If 10 lbs. Ammonia, per head per annum, from all sources.	
		1,000 tons Sewage = Guano.	1 ton Guano = Sewage.	1,000 tons Sewage = Guano.	1 ton Guano = Sewage.
Tons.	Persons.	Cwts.	Tons.	Cwts.	Tons.
40	25	$16\frac{1}{3}$	1220	13	1525
50	20	13	1525	$10\frac{1}{2}$	1900
60	$16\frac{2}{3}$	11	1830	$8\frac{2}{3}$	2290
80	$12\frac{1}{2}$	$8\frac{1}{2}$	2440	$6\frac{1}{2}$	3050
100	10	$6\frac{1}{2}$	3050	$5\frac{1}{4}$	3810
200	5	$3\frac{1}{4}$	6100	$2\frac{3}{4}$	7620
1 Person = Guano.		$\frac{2}{3}$ cwt.		$\frac{1}{2}$ cwt.	

Thus, with $12\frac{1}{2}$ lbs. of ammonia, and the minimum estimated dilution of the dry weather sewage at a rate of 40 tons per head per annum, 1,000 tons of such sewage would only contain nitrogen, reckoned as ammonia, equal to that in about $16\frac{1}{3}$ cwts. of Peruvian guano, or to that in only 13 cwts. if the amount of ammonia per head per annum be reckoned at only 10 lbs. In other words, in the former case it would require 1,220, and in the latter 1,525, tons of sewage to supply the ammonia (or nitrogen reckoned as ammonia) of 1 ton of guano. In like manner, taking 80 tons of sewage per head per annum as a minimum estimate for the average sewage, inclusive of rainfall, with $12\frac{1}{2}$ lbs. of ammonia per head per annum, 1,000 tons would represent the nitrogen of $8\frac{1}{2}$ cwts., and with 10 lbs., $6\frac{1}{2}$ cwts., of Peruvian guano; or reckoning $12\frac{1}{2}$ lbs. of ammonia per head per annum, 1 ton of Peruvian guano would represent 2,440 tons, and reckoning 10 lbs., it would represent 3,050 tons.

The table also shows that reckoning $12\frac{1}{2}$ lbs. of ammonia per head per annum, the sewage of an average individual would annually represent in nitrogen $\frac{2}{3}$ cwt., or reckoning only 10 lbs. per head per annum only $\frac{1}{2}$ cwt., Peruvian guano, per head per annum.

Crops to which Sewage is most applicable.

Hitherto, on grounds shown to be fully justified, we have, for simplicity of illustration, confined attention to the amount of nitrogen or ammonia in sewage, as the measure or indication of its composition, and of the theoretical manurial value of its total solid constituents. It is, however, obviously of interest to consider whether or not the mineral or incombustible constituents of sewage exist in it in sufficient proportion to the ammonia or nitrogen, for the requirements of the crops to be grown; and, as the phosphoric acid and potassa (the one or the other, or both, according to circumstances) are, perhaps, the mineral constituents most likely to be deficient relatively to the nitrogen, their proportion to the latter in sewage, and in various crops, may appropriately be referred to in illustration of the point. Table VII shows the proportion of phosphoric acid and potassa to 100 of nitrogen in sewage, according to the mean of ten analyses of the Rugby sewage, in which the phosphoric acid and the potassa as well as the ammonia were determined. It also shows what

may be taken as approximately representing the average proportion of phosphoric acid and potassa to nitrogen in various crops.

TABLE VII.

Amount of Phosphoric Acid and Potassa to 100 Nitrogen, in Sewage and in various crops.

Rugby Sewage	Phosphoric Acid.			Potassa.		
	27			42		
	In Corn, Roots, &c.	In Straw, Leaves, &c.	In Total Produce.	In Corn, Roots, &c.	In Straw, Leaves, &c.	In Total Produce.
Meadow-Hay	27	100
Clover-Hay	23	52
Wheat	48	42	46	28	108	57
Barley	40	34	38	34	126	60
Oats	28	37	30	25	155	65
Beans	25	46	30	32	123	50
Mangolds	17	100
Swedes	27	16	21	82	44	63
Common Turnips ..	28	18	26	160	71	117
Potatoes	42	123

It is obvious that since the phosphoric acid of sewage, like the nitrogen, will be derived almost exclusively from excretal matters and food-refuse, its proportion to the nitrogen will, within comparatively narrow limits, be tolerably uniform; the amount of potassa, on the other hand, will vary very much according to locality, and be considerably greater where the streets or roads are constructed of potassic minerals than elsewhere.

The table shows that, according to the analyses referred to, the Rugby sewage contained 27 parts of phosphoric acid and 42 parts of potassa, for 100 of nitrogen. It also shows that, on the average, meadow hay contains almost exactly the same proportion of phosphoric acid to nitrogen as the sewage, but a much greater proportion of potassa than the latter.*

In the cereal grains the proportion of phosphoric acid to

* According to Baron Liebig's estimates, hay contains 51 parts of phosphoric acid to 100 of nitrogen; but having collated and averaged the results of numerous independent observers, we can see nothing to lead to the adoption of such a figure; whilst direct determinations in a number of samples of each, showed in the Rugby sewaged grass 25, and in the unsewaged 32 parts.

nitrogen is, on the other hand, higher than in the sewage; whilst in most of the other crops enumerated it is much about the same. Of potassa, the proportion is lower in the cereal grains (the only part of the crop which is, as a rule, sold off the land) than in the sewage, though in the other crops it is generally higher.

But there are various circumstances, the adequate discussion of which would occupy more space than it would be appropriate to devote to their consideration here, which render it quite inadmissible to draw direct practical conclusions as to the applicability of sewage to different crops from what may appear, at first sight, the obvious indications of the figures in the table. Nevertheless, a careful consideration of the subject leads to the conclusion that, if sewage alone were applied constantly to meadow land, potassa would be more likely to become deficient than phosphoric acid; but that, if it were applied to the ordinary crops of rotation, phosphoric acid would be more likely to become deficient than potassa. Still, granting it to be clearly shown that with this or that description of soil or management, town-sewage was, in proportion to its nitrogen, deficient in this or that constituent for the production of this or that crop, or crops generally, it would by no means follow that it was an inappropriate manure on that account; for, any defect in composition, whether in regard to phosphoric acid, potassa, or any other constituent, could be easily compensated from other sources.

Indeed, independently of what we know of the sources of the constituents of sewage, and can judge therefrom of their appropriateness as manure for different crops, there is nothing in the results of the analysis of the solid matter of sewage, from which we should be justified in concluding that it is not applicable as manure to crops generally. On the contrary, a dry and portable manure, having the composition of the solid matter of town-sewage, would undoubtedly be generally applicable both to corn and other rotation crops, and to grass; and its constituents could then fairly be valued by the same scale as other concentrated manures in the market.

But the great dilution of town sewage, its large daily supply at all seasons, and its greater amount in wet weather when the land can least bear, or least requires, more water, render it extremely inappropriate for application on a comprehensive scale to arable land, for the growth of corn and other ordinary rotation crops.

But, apart from these difficulties, if sewage can only be distributed in small quantities over large areas, at such a cost to the farmer as has yet been proposed, it is indeed vain to hope that any large proportion of the manurial constituents, derived from the consumption of human food in our towns, can be redistributed over the area from which they came; for such is the limit set by climate to the amount of manure and of water applicable for crops that have to ripen their seed, that, for corn more especially, only comparatively small quantities per acre could be employed, and hence, were sewage systematically applied for their growth, the area of utilization must necessarily be very large. On this point it may be stated that Mr. Rawlinson, one of the members of the Royal Sewage Commission, has given it as his opinion that it would cost more to distribute 500 tons of sewage per acre, by means of pipes, hydrants, and hose and jet, as would be requisite in the case of application to arable land and crops generally, than to apply 5,000 tons per acre by means of open runs, as in the case of its application to grass.

From these considerations it will be obvious, that that which may be called the theoretical value of sewage, reckoned according to the constituents it contains, is not necessarily its practical or available value when used in its highly diluted condition. It will be also obvious, that in that condition it is the most appropriate for grass, for which it can be employed at all seasons, and in comparatively large quantities on a limited area, and that it is the least appropriate for crops which have to ripen. The question arises—what is the practical or realizable value of the constituents of sewage when they are utilized in the condition of dilution in which they exist in that fluid? This point will be illustrated by reference, both to the results of direct experiments, and to the experience of practical men who have utilized sewage with a view to profit.

Results of direct Experiment on the Utilization of Sewage.

At Rugby two fields of meadow land were experimented upon; in each one plot was left without sewage, one received sewage at the rate of 3,000 tons, one at the rate of 6,000 tons, and one at the rate of 9,000 tons, per acre per annum. The experiments were so conducted through three consecutive seasons, and Table VIII summarizes the results obtained.

TABLE VIII.

Quantities of Sewage applied, and of Green Grass obtained, per acre per annum, in Experiments made at Rugby.

Seasons 1861, 1862, and 1863.

Seasons.	Plot 1. Unsewaged.	Plot 2. 3,000 Tons Sewage.	Plot 3. 6,000 Tons Sewage.	Plot 4. 9,000 Tons Sewage.
Grass obtained. Five-Acre Field.				
1861	Tons. cwt. qrs. lbs. 9 5 3 5	Tons. cwt. qrs. lbs. 14 16 3 8	Tons. cwt. qrs. lbs. 27 1 0 10	Tons. cwt. qrs. lbs. 32 16 3 8
1862	8 3 1 10	27 18 0 18	34 10 0 19	32 9 2 22
1863	4 18 3 13	22 5 0 11	34 18 1 27	37 0 2 5
Average....	7 9 1 9	21 13 1 12	32 3 1 0	34 2 1 12
Ten-Acre Field.				
1861	8 18 0 15	15 16 3 2	22 15 2 12	26 13 3 12
1862	16 10 0 25	27 11 0 20	32 2 1 14	31 12 1 20
1863	8 0 3 19	25 5 1 8	30 11 2 12	34 19 1 21
Average....	11 3 0 10	22 17 3 1	28 9 3 13	31 1 3 18
Averages :—the three years and both Fields.				
1861, 2, and 3	9 6 0 24	22 5 2 7	30 6 2 6	32 12 0 15

The five-acre field was much flatter than the other; its soil and subsoil were much more porous; the mechanical and chemical examination of samples, taken to the depth of 9 inches, showed its soil to be much more stony, to retain much less water under equal external conditions, to contain much less organic matter, much less nitrogen, much less clay, and much more sand, than that of the ten-acre field. It was, in fact, considerably inferior in natural quality, and yielded, accordingly, considerably less produce without manure. Notwithstanding this, it will be seen that it gave upon the whole more total produce per acre under the influence of sewage than did the naturally better soil of the ten-acre field; and, it will be shown further on, that the sewage was in its case both more completely utilized and more completely purified.

It would be inappropriate to discuss in detail here the influence of season and other circumstances upon the produce of the different years or the respective plots. It will be sufficient to call attention to the general character of the results, and to the practical conclusions to which they seem to lead. By the application of sewage a supply of green food was obtained much earlier and much later in the season, and the total quantity per acre was increased several fold. There was, generally, though not invariably, the more produce the greater the amount of sewage applied, the exceptions being in the wet and cold season of 1862. In the other seasons, and in both fields, there was an increase of produce with each increase in the amount of sewage applied; and the largest amounts of produce obtained at all were, in both fields, in the third season of application, and on the plots which had received the largest amounts of sewage. Still, it is important to remark, that the amounts of increase of produce for a given amount of sewage applied were the less where the larger quantities were employed. Experience abundantly shows, indeed, that if the only object were to get the largest possible amounts of produce per acre, as much as 30,000, 40,000, or even 50,000 tons of sewage might frequently be applied per acre with advantage; but under such conditions the sewage would be very inadequately both utilized and purified, and a minimum amount of increase would be obtained for a given amount of sewage applied.

Looking, however, both to urban and to rural interests, and to purification as well as utilization, much more moderate applications than such as are required to yield the greatest amount of produce per acre, must be had recourse to. By way of practical suggestion on this point it may be stated that, on consideration of the circumstances under which the amounts of produce recorded in the Table were obtained, it is concluded that with an application of about 5,000 tons of average sewage per acre per annum, applied as it must be, pretty evenly throughout the year, there might be expected, taking the average of soils and seasons, an average of about 30 tons of grass. Assuming such a produce, and allowing £4 per acre for rent or natural yield, the grass would, if sold for 10s. per ton, give a gross return of 0·53d. per ton of sewage employed, if for 12s. 6d. per ton 0·7d., and if for 15s. per ton, 0·9d. From these amounts there would, of course, have to be deducted the cost of main distribution and application of the sewage, other expenses of the crop, and the farmer's profit, before

anything was available as payment to the town for the manurial matters.

In comparison with the result here assumed it may be observed that in the neighbourhood of Croydon, where about 250 acres are laid down for sewage irrigation, and where there are probably more than 6,000 tons of sewage annually available for each acre, from 25 to 30 tons of meadow grass, selling for from £20 to £25, are obtained per acre per annum; and after deducting as before £4 for rent, the gross return per ton of sewage employed is from 0.6d. to 0.8d. With a somewhat similar application to Italian rye-grass, 30 to 35 tons, selling for from £25 to £30 are obtained, yielding, after deduction for rent or natural produce, from 0.8d. to 1d. per ton of sewage employed. It will be observed that in these cases the selling price of the grass is 16s. or 17s. per ton; but it is obvious that if sewage were extensively employed for the production of grass, its present price could not be maintained.

A marked effect of liberal sewage irrigation (indeed of active manures generally), on the mixed herbage of grass land, is greatly to develop the Gramineous plants, nearly to exclude the Leguminous, and to reduce the prevalence of miscellaneous or weedy plants, but much to encourage individual species. Among the grasses, according to locality or other circumstances, the rough meadow grass (*Poa trivialis*), couch grass (*Triticum repens*), rough cock's foot (*Dactylis glomerata*), woolly soft grass (*Holcus lanatus*), and perennial rye-grass (*Lolium perenne*), have been observed to become very prominent; two or three only remaining in any considerable proportion after some years of liberal sewage application. But sewaged produce being generally cut or grazed comparatively young, the tendency which the great luxuriance of a few very free-growing grasses has to give a coarse and stemmy later growth is not an objection, as in the case of meadows left for hay.

The chemical examination of the grass grown at Rugby showed that, at the stage of growth at which it was cut, the sewaged grass contained a less proportion of dry or solid substance than the unsewaged; that the grass cut during the later portions of the season (both unsewaged and sewaged) contained less solid matter than that cut during the more genial periods of growth; that the proportion of nitrogenous substance (and also of impure fatty or waxy matter) was much greater in the solid matter of the sewaged than in that of the unsewaged grass; that the proportion of nitrogenous substance was also much higher in the

solid matter of the grass grown towards the end than earlier in the season; that the proportion of indigestible woody-fibre was much about the same in the dry substance of the unsewaged and of the sewaged grass, but progressively diminished as the season advanced; and, lastly, that a given amount of the dry substance of grass grown in a cold and wet season, or during the cold and wet periods of the year, generally contained more nitrogenous substance than that of grass grown in more genial weather.

It will be seen presently, that, with these differences in botanical and chemical character between the unsewaged and the sewaged grass, when used as food, a given quantity of the fresh unsewaged grass was more productive of both meat and milk than an equal weight of the fresh sewaged grass; but that a given weight of the dry or solid substance of the sewaged grass was more productive than an equal weight of that of the unsewaged. Further, the less nitrogenous grass of the more genial periods of the season was more productive than the more highly nitrogenous produce of the less genial periods.

Experiments were made at Rugby with Italian rye-grass as well as meadow-grass, but the results were not sufficiently distinct in their character from those above described to render it of much interest to consider them in this place.

The next points to consider are—the comparative food-qualities of unsewaged and sewaged grass, and the best or most profitable mode of utilizing sewage-irrigated grass.

When in the experiments at Rugby the grass was cut green, and given to fattening oxen tied up under cover, more of the sewaged than of the unsewaged, reckoned in the fresh or green state, was both consumed by a given weight of animal within a given time, and required to produce a given weight of increase; but of real dry or solid substance, less of that of the sewaged than of the unsewaged grass was required to produce a given effect. When the grass was given alone the result was very unsatisfactory, but when oilcake was given in addition, the amount of increase upon a given weight of animal within a given time, and for a given amount of dry substance of food consumed, was not far short of the average result obtained when oxen are fed under cover on a good mixed diet. Still, the pecuniary result with the oxen, whether reckoned per acre or for a given amount of sewage, was by no means satisfactory.

It should here be mentioned that, at Croydon, although the land there was more liberally irrigated than at Rugby, much more satisfactory results have been obtained with fattening stock fed on the land. The practice there is, to irrigate for three or four days and nights together, to repeat the treatment two or three times for each crop, and, when the grass has got a sufficient head, to stop the application and turn the stock upon the land, where they remain until the grass is closely eaten down. They are then removed, the land is re-irrigated, and so on.

Very much better results were obtained at Rugby when the grass was given to milking cows. Referring to the Report of the Sewage Commission for all further details, the summary of the results with cows given in Table IX will suffice for consideration here.

TABLE IX.

Results obtained at Rugby, with Cows fed on Unsewaged and Sewaged Grass, in 1861, 1862, and 1863.

	Plot 1. Unsewaged.	Plot 2. 3,000 Tons Sewage.	Plot 3. 6,000 Tons Sewage.	Plot 4. 9,000 Tons Sewage.
Time each acre (with oilcake, if any) would keep 1 cow :—				
	Weeks.	Weeks.	Weeks.	Weeks.
1861—Grass (alone).....	19	41	59	69
1862—Grass (with oilcake).....	42	63	73	72
1863—{ Grass $\frac{1}{2}$ without, $\frac{1}{2}$ with oilcake }	22	48	67	73
Means..	28	51	66	71
Milk from the produce of each acre (exclusive of oilcake,* if any) :—				
	Gallons.	Gallons.	Gallons.	Gallons.
1861—Grass (alone).....	321	571	820	961
1862—Grass (with oilcake).....	613	835	973	958
1863—{ Grass $\frac{1}{2}$ without, $\frac{1}{2}$ with oilcake }	414	876	1207	1327
Means..	449	761	1000	1082
Value of milk from the produce of each acre (exclusive of oilcake*, if any), at 8d. per gallon :—				
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
1861—Grass (alone).....	10 14 3	19 0 6	27 6 11	32 0 10
1862—Grass (with oilcake).....	20 8 10	27 16 10	32 8 11	31 18 10
1863—{ Grass $\frac{1}{2}$ without, $\frac{1}{2}$ with oilcake }	13 16 0	29 3 9	40 4 7	44 4 4
Means..	14 19 8	25 7 0	33 6 10	36 1 4

TABLE IX (*continued*).

	Plot 1. Unsewaged.	Plot 2. 3,000 Tons Sewage.	Plot 3. 6,000 Tons Sewage.	Plot 4. 9,000 Tons Sewage.
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Increased produce of milk per 1,000 tons sewage applied (exclusive of oilcake,* if any) :—

		Gallons.	Gallons.	Gallons.
1861—Grass (alone).....		180	178	151
1862—Grass (with oilcake)		74	60	38
1863—{ Grass ($\frac{1}{2}$ without, $\frac{1}{2}$ with } oilcake		154	132	101
Means..		136	123	97

Increased value of milk (at 8*d.* per gal.) per 1,000 tons sewage applied (exclusive of oilcake,* if any) :—

		£ s. d.	£ s. d.	£ s. d.
1861—Grass (alone).....		5 19 10	5 18 8	5 0 11
1862—Grass (with oilcake)		2 9 4	2 0 0	1 5 7
1863—{ Grass ($\frac{1}{2}$ without, $\frac{1}{2}$ with } oilcake		5 2 7	4 8 1	3 7 7
Means..		4 10 7	4 2 3	3 4 8

It may be stated generally, that when the cows were fed on grass alone, as much as they chose to eat, a given weight of the animal was more productive, both of milk and increase, but especially of milk, on the unsewaged than on the sewaged grass. More milk was also produced from a given weight of the unsewaged grass, reckoned in the fresh or green state, than from an equal weight of the fresh sewaged grass. Of dry or solid substance, however, a given weight of that of the sewaged grass produced, on the average, more milk than an equal weight of that of the unsewaged.

The milk from the cows fed on the sewaged grass was, upon the

* The *value* of the milk, "exclusive of oilcake," is reckoned by deducting the cost of the cake consumed, less the estimated value of the manure it yields, from the gross value inclusive of oilcake; and the *amount* of milk, "exclusive of oilcake," by deducting from the gross amount of milk with oilcake at the rate of one gallon for every 8*d.* of deducted value. Such estimates are, however, obviously only approximations to the truth.

whole, slightly the less rich, containing generally somewhat less casein, butter, sugar, and total solid matter (though more mineral matter) than that from the unsewaged; but when oilcake was given with the grass, whether sewaged or unsewaged, the richness of the milk was notably increased.

The productive quality of the grass was very different in different seasons, and at different periods of the same season, being very inferior in the wet and cold season of 1862, and towards the close as compared with the earlier periods of the seasons.

Without commenting further on the difference of result obtained under different conditions of season, or under other varying circumstances, it will be sufficient briefly to call attention to the more general results which the records in the table bring prominently to view, and to the practical conclusion which, on a careful consideration of all the circumstances and details, may seem to be safely deducible from them.

It is seen that whether we reckon the total amount of food yielded per acre, or the amount, or the value, of the milk obtained from the consumption of the produce of each acre, there was a very great increase, varying from two to three-fold, according to season, by the use of sewage. The land upon which these experiments were made was good feeding pasture, of probably more than average quality, and the natural yield, without sewage, was, therefore, correspondingly high. Taking into consideration this fact, and other circumstances under which the results were obtained, it is concluded that, if not larger amounts of total produce per acre, at any rate larger amounts of increase for a given quantity of sewage may be expected when it is applied systematically over large tracts of land, with a view to the production of grass and milk.

It is estimated that with 5,000 tons of sewage per acre per annum, judiciously applied to Italian rye-grass or meadow-land properly laid down to receive it, an average *gross* produce of not less, and perhaps more, than 1,000 gallons of milk per acre per annum might be anticipated; and it may be observed that 1,000 gallons of milk at 8d. per gallon would represent a *gross* money return of £33 6s. 8d.

Putting the result in another way it may be stated that it required, according to circumstances, the consumption of between 5 and 6 tons of grass for the production of 1 ton of milk; and if we reckon 6 parts of grass for 1 of milk, and 30 tons of grass per

acre, this would give a *gross* return in value of milk at 8d. per gallon of something over £37 per acre, or of about 25s. per ton, of grass consumed.

Still another illustration of the important bearing of the question of the utilization of the sewage of our town populations upon the re-production of food may be given. Supposing the whole of the sewage of a given population (which, however, would seldom be the case) were applied exclusively for the growth of grass for the production of milk, the result would be an increased yield of about $2\frac{1}{2}$ pints of milk per week, or about $\frac{1}{2}$ lb. per day, per head of such population. So far as the sewage were so applied, a portion of the milk produced would, of course, be represented, in consumption, by its equivalent in butter and cheese. A portion of the grass would, however, be used directly for the production of meat; and, in addition to the milk and meat produced by the consumption of the grass, a large amount of solid manure would be obtained, which would be applicable to arable land for the growth of corn and other rotation crops.

It would appear, then, that if town sewage were to a great extent utilized by the application of something like 5,000 tons per acre per annum to Italian rye-grass and meadow-land, a direct result would be a very greatly increased production of important articles of human food which are at present both scarce and dear. But the question remains—would the sewage, by such an application, be sufficiently purified to allow of the drainage from the irrigated land being turned into rivers which are to be used as a water-supply for other towns? Some light will be thrown on this subject by the results next to be considered.

In order to determine how far, in the experiments at Rugby, the sewage was deprived of its manurial or putrescible constituents in its passage over and through the land, samples of the drainage water were collected for analysis in each field, simultaneously with those of the sewage, commencing in May, 1862, and ending in October, 1863. In all 62 partial analyses of drainage-water, corresponding in detail with those of the sewage, were made. A few other analyses, in much more detail, were made of the sewage and drainage of the season of 1864. The results of the large number of partial analyses are summarized in Table X, which shows, in parallel columns, the average composition of corresponding samples of sewage and drainage.

TABLE X.

Mean Composition of the Rugby Sewage before application, and of the Drainage-water from the Irrigated Land, in the Seasons 1862 and 1863.

Grains per Gallon.

Constituents.	Five-Acre Field.		Ten-Acre Field.		The two Fields.	
	Sewage.	Drainage.	Sewage.	Drainage.	Sewage.	Drainage.
Season 1862; May—October, both inclusive.						
In suspension	11 Samples.	8 Samples.	11 Samples.	11 Samples.	22 Samples.	19 Samples.
	Inorganic... 25·67	1·81	24·89	3·74	25·28	2·92
	Organic... 14·69	1·40	17·14	1·39	15·92	1·39
	Total... 40·36	3·21	42·03	5·13	41·20	4·31
In solution ...	Inorganic... 34·49	34·50	32·38	37·10	33·44	36·01
	Organic... 7·83	7·18	7·66	7·83	7·71	7·56
	Total... 42·32	41·68	39·98	44·93	41·15	43·57
	Total inorganic ... 60·16	36·31	57·27	40·84	58·72	38·93
	Total organic..... 22·52	8·58	24·74	9·22	23·63	8·95
	Total solid matter... 82·68	44·89	82·01	50·06	82·35	47·88
Ammonia	In suspension 1·37	0·24	1·52	0·33	1·44	0·29
	In solution ... 4·13	0·80	4·26	1·85	4·20	1·41
	Total... 5·50	1·04	5·78	2·18	5·64	1·70
Season 1863; November, 1862—October, 1863, both inclusive.						
In suspension	23 Samples.	21 Samples.	22 Samples.	22 Samples.	45 Samples.	43 Samples.
	Inorganic... 39·41	2·14	34·93	3·93	37·22	3·06
	Organic... 27·35	1·41	25·99	3·29	26·69	2·37
	Total... 66·76	3·55	60·92	7·22	63·91	5·43
In solution ...	Inorganic... 39·57	38·55	38·77	41·35	39·18	39·98
	Organic... 8·35	7·46	8·30	7·98	8·32	7·73
	Total... 47·92	46·01	47·07	49·33	47·50	47·71
	Total inorganic ... 78·98	40·69	73·70	45·28	76·40	43·04
	Total organic 35·70	8·87	34·29	11·27	35·01	10·10
	Total solid matter... 114·68	49·56	107·99	56·55	111·41	53·14
Ammonia	In suspension 2·08	0·15	1·98	0·31	2·03	0·23
	In solution ... 5·83	0·69	5·69	1·85	5·76	1·28
	Total ... 7·91	0·84	7·67	2·16	7·79	1·51

It is seen that of matter in suspension in the sewage, nearly the whole, both inorganic or organic, was retained by the soil; and probably a considerable part of the little which the drainage-water contained was derived from the soil itself.

Of matter in solution, on the other hand, a gallon of the

drainage-water contained, on the average, much about the same amount, both inorganic and organic, as a gallon of the sewage; though, doubtless, a considerable portion of the soluble matters in the drainage had their immediate source in the soil—the sewage giving up valuable manurial matters to the soil, and the fluid in its turn taking up substances from it.

It is important to remark that the drainage from the more porous and less naturally fertile soil of the five-acre field (which, however, gave the largest amount of increase for a given amount of sewage), contained less of almost every constituent, or class of constituents, enumerated, than did that from the more argillaceous and more naturally fertile soil of the more steeply sloping ten-acre field. The result is particularly marked in the case of the ammonia. The fact here indicated is of considerable practical, as well as scientific, interest; and it is perfectly consistent with the results of common experience, which tend to show that a soil which may contain a comparatively small proportion of clay, but which is thoroughly porous, is, as a rule, much better adapted for sewage irrigation, both as regards the utilization and the purification of the sewage, than one which, though richer in clay and of higher natural quality, is but imperfectly permeable by the fluid.

The results given in Table XI show in more detail the changes in the composition of the fluid in its passage through the soil. They relate to samples of sewage and drainage taken in another field at Rugby, during very dry weather, in the summer of 1864. The plan of collection was, to take of sewage about a gallon, and of drainage about half a gallon, eight or ten times during the ten or twelve working hours of the day; at the end of the day, after well shaking, to take a gallon from each mixture; and to repeat this for six consecutive days, until six gallons of each were obtained, when, after well shaking, a two-gallon sample of each was bottled off for the purposes of analysis.

TABLE XI.

Detailed Composition of samples of the Rugby Sewage before application, and of the Drainage-water from the irrigated land, collected July, 1864.

Constituents.		Grains per Gallon.			
		Collected July 6—11.		Collected July 13—18.	
In suspension.	Inorganic matter:—	Sewage.	Drainage.	Sewage.	Drainage.
	Oxide of iron and alumina.....	4·57	..	6·30	..
	Lime.....	4·48	..	3·75	..
	Magnesia.....	0·65	..	0·25	..
	Carbonic acid.....	3·25	..	2·17	..
	Phosphoric acid.....	1·84	..	1·14	..
	Silica, sand, &c.....	31·60	..	39·30	..
	Total.....	46·39	..	52·91	..
	Organic matter.....	40·40	..	32·40	..
	Total matter in suspension..	86·79	..	85·31	..
In solution.	Inorganic matter:—	Traces.	..	1·25	0·25
	Oxide of iron, &c.....	8·45	10·25	8·23	10·08
	Lime.....	1·76	1·69	1·80	1·69
	Soda (1).....	5·46	0·38	5·24	2·30
	Chloride of sodium (1).....	6·82	9·73	8·53	9·21
	Chloride of potassium (1).....	6·08	1·50	6·17	2·34
	Sulphuric acid.....	4·39	6·55	4·01	6·75
	Phosphoric acid.....	1·28	0·44	1·66	0·32
	Carbonic acid.....	8·83	6·18	7·42	7·01
	Silica.....	1·80	0·80	1·00	0·80
	Total.....	44·87	37·52	45·31	40·75
	Organic matter.....	11·20	7·80	10·00	7·05
	Total matter in solution....	56·07	45·32	55·31	47·80
Total inorganic matter.....		91·26	37·52	98·22	40·75
Total organic matter (2).....		51·60	7·80	42·40	7·05
Total solid matter.....		142·86	45·32	140·62	47·80
(1) Containing	Potassa.....	3·84	0·94	3·90	1·48
	Soda.....	9·07	5·54	9·76	7·17
	Chlorine.....	7·03	6·61	8·10	6·70
(2) Containing	Ammonia {	In suspension.....	2·92	..	2·42
		In solution.....	5·74	0·98	6·36
		Total.....	8·66	0·98	8·78
	Nitric acid in solution = Ammonia.....		(3) 1·33	..	(4) 1·41

(3) 4·227 Nitric acid = 1·096 Nitrogen = 1·331 Ammonia

(4) 4·483 " = 1·162 " = 1·411 "

The soil was light and gravelly, with a gravelly subsoil; but an examination of the figures in Table XI shows, that it had done the work of absorption, at any rate as well as, if not better than, on the average, did the soils in the other fields. It was intended to take samples for detailed analysis from this field under various conditions of the weather, but owing to the continuance of the drought, this could not be accomplished.

In judging of these results, as well as those already considered, it must, of course, be borne in mind that, excepting when the land is already saturated with water, a gallon of drainage will represent much more than a gallon of sewage; and that, hence, the amount of any constituent of the sewage found in a gallon of the drainage must have been derived from more than a gallon of the former. The non-retention of valuable manurial matters by the soil was, therefore, not so great as would at first sight appear on an inspection of the comparative composition of equal volumes of the sewage and of the drainage.

As in the larger number of cases, so in these, the quantity of matter in suspension in the drainage was very small, and being obviously in great part derived from the soil, it was not submitted to quantitative analysis. A considerable proportion of the phosphoric acid of the sewage was in suspension, but there was none of it in suspension in the drainage, the whole of the portion so existing in the sewage having been retained by the soil.

It is satisfactory to observe that among the inorganic constituents in solution in the sewage, by far the larger proportion of those which are, perhaps, the most likely to become relatively deficient, was retained by the soil. Thus, smaller proportions of both the potassa and the phosphoric acid of the sewage passed off in the drainage than of any other constituents. Soda was also retained by the soil to a considerable extent, magnesia in a less degree, and lime less still. Of lime, indeed, there was more in a gallon of drainage than in a gallon of sewage; of sulphuric acid also there was considerably more in the drainage than in an equal volume of the sewage. Lastly, of soluble silica a notable portion passed off in the drainage.

Of organic matter in solution a very considerable quantity was found in the drainage-water. The character of the soluble organic matter in the drainage is, however, very different from that in the sewage. It contains very much less ammonia, or ammonia-yielding matter; and, especially in periods of active vegetation, will,

doubtless, frequently be derived from vegetable matter within the soil, rather than directly from the sewage.

A very important point to remark is, that, whilst the sewage scarcely contained an appreciable amount of nitric acid, the drainage contained more nitrogen in that form than as ammonia; the result being that the soil had retained a considerably less proportion of that important manurial constituent of the sewage than would have been supposed had only the more partial analyses been made.

The general result was, that, practically, the whole of the insoluble or suspended matter of the sewage was retained by the soil; and that, of the constituents of the sewage, whether in suspension or in solution, those which are of the most value, because the most liable to become relatively exhausted, were the most efficiently retained. Nevertheless, the drainage-water still retained so much of potassa, phosphoric acid, ammonia, and nitric acid, as clearly to show that the sewage had not been perfectly deprived of its valuable manurial matters, and also so much of total soluble matter, especially of soluble organic matter, as to show that it had not been by any means perfectly purified.

There is, indeed, a limit to the power which a soil possesses of removing substances from solution, or of preventing those already absorbed from being dissolved in water passing through it, the result being dependent on the physical and chemical characters of the soil itself, and on the amount and composition of the fluid passing through it. So far as the soluble organic matters of the drainage are derived from vegetable matter within the soil, it is a question whether there will not always be a considerable amount in that passing from land covered with luxuriant vegetation. So far, however, as the nitrogen of the drainage exists in the form of nitric acid, it is a pretty satisfactory indication that the organic matter has, to a great extent, already passed the stage of deleterious putrescence.

In the Rugby experiments the arrangements were not such as to allow of the water drained from one portion of the land being passed over another; but at Beddington, near Croydon, a great portion of the water does duty twice, and sometimes three times; and from results kindly communicated by Mr. Latham, the engineer to the Croydon Board of Health, and given in the following table, it would appear that there the water eventually passes from the land in a state of much greater purity than was the case in the Rugby experiments.

TABLE XII.

Partial Analyses of the Croydon Sewage before application, of the Drainage-water from the irrigated land, and of the River Wandle, above and below the Drainage Outfall from the irrigated land.

Constituents.	Croydon.		River Wandle.	
	Sewage.	Drainage.	Above Drainage Outfall.	Below Drainage Outfall.
	Grains per gallon.			
Inorganic matter	48·30	23·40	18·56	20·16
Organic matter	52·20	2·40	1·44	2·08
Total solid matter ..	100·50	25·80	20·00	22·24
Ammonia	6·70	0·21	0·18	0·18

The figures show much about the same amount of ammonia in the sewage of Croydon, as was found on the average in that of Rugby; but the amount in the Croydon drainage was extremely small. It is unfortunate that the quantity of nitric acid was not also determined; but we are informed that it undoubtedly exists in some amount in the drainage from the Beddington meadows. Still, although formerly the Croydon Board had to meet numerous law-suits on account of the pollution of the river by the sewage, the fluid is now so far purified before being discharged, that those having the right of fishing in the river have found it worth while to fix gratings to prevent the fish going up the main outfall from the sewage-irrigated land.

The results obtained in regard to this part of the subject—that of purification—however interesting and important, must still be looked upon as little more than initiative; but there can be no doubt that, when large quantities of sewage are applied to grass-land, the arrangements should be such as to allow of the drainage-water being collected and re-used in such a manner as to insure as far as possible both complete utilization and complete purification. It must be admitted, however, that further experience, and further investigation, are still wanting, to determine what amount of sewage, provided the drainage-water be properly re-distributed, can be

safely applied to a given area, under different conditions of soil and subsoil, and under different conditions of season, so as to insure its sufficient purification.

Experience of Common Practice in the Utilization of Sewage.

Leaving the results of experimental inquiry, it will be well briefly to notice those of practical experience hitherto, in regard to the value and utilization of town sewage. The instance most frequently quoted is that of the neighbourhood of Edinburgh, relating to which some particulars are given in the following Table :—

TABLE XIII.

Relating to the Sewage-irrigated Meadows near Edinburgh.

Names of Meadows.	Imperial Acres under Irrigation.	Approximate Population contributing to each Acre.	Approximate Quantity of Sewage available for each Acre.
Lochend, Spring Gardens and Craig-entinnay }	285	337	Tons. 20,500
Roseburn and Western Dalry	80	112	17,000
Quarry Holes	8	562	65,000
Broughton Burn	6	1,666	102,000
The Grange	16½	302	97,000

These tabular statements are chiefly based upon direct information, obtained in part from Mr. McPherson, the Edinburgh City Surveyor, and in part from the occupiers or managers of the respective meadows. To prevent misunderstanding, however, it must be explained with regard to them, that, as water-closets are not universal, and as the sewage is frequently allowed to pass unused, the records of the amount of population contributing to, and of sewage available for, each acre, do not show the amounts actually utilized, but only approximately the total amounts available, whether used or wasted.

Sewage has been applied to some portions of the land in the neighbourhood of Edinburgh for about 200 years, to a considerable portion for more than 60, and to most of that now under irrigation for more than 30 years. In two instances arrangements have been made for raising the sewage, by pumping, an inconsiderable

number of feet; but the cost has been found too great to allow of a sufficient quantity being applied per acre, and hence the application in this way has been much limited, if not on some portions of the land entirely abandoned. The application is confined to meadow land and Italian rye-grass, and the distribution is entirely by means of open runs. When Italian rye-grass is grown, the land is periodically broken up, and one or two other crops taken without sewage before laying down again to grass. The application to ordinary rotation crops on arable land forms no part of the system adopted.

There is no doubt that at Edinburgh larger amounts of sewage are applied per acre than anywhere else, and that it is under those conditions that there are there obtained larger amounts of produce per acre than anywhere else. Nor is there any doubt, on the other hand, that there is, at Edinburgh, not only very great waste of manurial constituents, but very imperfect purification of the sewage. Hence the experience there, however interesting and important in some points of view, cannot be taken as the foundation either of estimates of the value realizable in practice by the utilization of given amounts of sewage, or of the sewage of a given population, or of safe conclusions as to the amount of sewage that can advantageously be applied per acre when the drainage has to be passed into a river, which may have to serve as the water-supply of other towns, instead of, as at Edinburgh, having an immediate outfall into the sea.

It may be mentioned that generally four or five crops of grass are obtained per acre annually, amounting, according to circumstances, to 30, 40, 50, 60, and even more tons per Imperial acre, and selling for prices varying from £8 to over £10 per acre, but averaging perhaps about £25. These results are, indeed, sufficiently striking, and well merit careful inquiry and consideration; but, for the reasons above stated, the exact practice of Edinburgh is not applicable to towns generally, and is especially inapplicable to inland towns.

Table XIV summarizes the results of the experience of the most important instances of sewage utilization in other localities.

TABLE XIV.

Relating to Sewage-irrigation in various localities.

Towns.	Population contributing.	Acres.		Crops, &c.	Annual Payment to Towns.
		Original.	Reduced.		
Alnwick	6,500	270	0	Arable and grass ; abandoned	Nothing
Carlisle	22,000	70	..	Meadow-grass ; all grazed	?
Croydon	16,000	250	..	Meadow and rye-grass	£300
Malvern	4,000	50	..	Grass	Nothing
Rugby	6,700	{ 190 280	20 100	Meadow and rye-grass Meadow ; chiefly grazed	} £50
Tavistock....	6,000	95	..	Grass	Nothing
Watford ...	4,000	210	{ 7 35	Rye-grass—Summer Meadow grass—Winter	} £10
Worthing ..	7,000	42	..	Grass ; not yet at work	Nothing

At Alnwick, the late Duke of Northumberland put down machinery and piping for the distribution of the sewage of the town over about 270 acres of mixed arable and grass land. After a very short time, the tenants, who had the free use of the sewage for the cost of its application, abandoned it altogether ; and the Bailiff of the District, who reports the failure, expresses his opinion strongly against the general applicability of sewage to arable land.

At Carlisle, the sewage of only a portion of the town is utilized. It is deodorized by Mr. McDougall's disinfecting fluid, and raised by steam power some 10 or 12 feet into an open cut, from which it is diverted for application to the land by moveable iron troughs. It is estimated that from 8,000 to 9,000 tons of sewage are applied per acre per annum. It is understood that little or nothing is realised by the town ; but that the tenant makes a considerable profit by sub-letting the sewage-irrigated land for grazing purposes.

In the neighbourhood of Croydon, as already referred to, the sewage of nearly 20,000 persons is applied to about 250 acres of meadow and Italian rye-grass. It is calculated that more than 6,000 tons of sewage are available for each acre. A considerable portion of the fluid is used two or three times over ; and it finally

passes from the land pretty satisfactorily purified. It is estimated that, after making deduction of £1 for rental, the *gross* return per ton of sewage applied is, at the present prices of the produce, with Italian rye-grass from $\frac{3}{4}$ d. to 1d., and with meadow grass from $\frac{1}{2}$ d. to $\frac{3}{4}$ d. The sewage is not applied in any systematic manner to other crops, but it has been tried on a small scale to root-crops. An enlargement of the area of irrigation is contemplated, which will, if carried out, somewhat reduce the amount of fluid and excretal matters available per acre below the quantities above stated.

About 12 years ago, arrangements were made for collecting the sewage of Rugby in a tank, from which it is pumped, by a 12-horse power engine, through iron pipes laid down for the distribution over about 470 acres of mixed arable and grass land. Up to last year 190 acres were held by Mr. James Archibald Campbell, but he has gradually limited the area of application, and during the last few years has abandoned the use of hose and jet, excepting occasionally on a small scale, and confined the application almost exclusively to from 12 to 20 acres of meadow and Italian rye-grass. The remainder of the land, amounting to about 280 acres, has passed through the hands of two tenants, both of whom are said to have sustained considerable loss. The last of the two had confined the application almost exclusively to about 100 acres of grass land, and applied the sewage almost entirely by open runs. The whole is now in the hands of the landlord, Mr. G. H. Walker, who, it is understood, is contemplating the abandonment of the use of steam power, pipes, and hose and jet, and the application to a limited area by means of gravitation.

The general result at Rugby is, then, that after about a dozen years of practical experience, with arrangements adapted for the application of small quantities of sewage per acre, to arable as well as to grass land, and to all crops, the area has been greatly limited, the use to any other crops than meadow and Italian rye-grass is quite exceptional, and the application by means of steam-power, pipes, and hose and jet, will probably soon be entirely abandoned. It may be added that, at the time of the experiments of the Commission, the sewage, which was considerably stronger than that of the Metropolis, cost the tenants only about $\frac{3}{4}$ d. per ton at the hydrants in the fields; yet, rather than incur the loss of using it at that cost, both were glad to get rid of it to the Commission, at rates which, though three times as high during the

six summer as during the six winter months, averaged the year round scarcely, but very nearly, 1d. per ton at the hydrants.

Some years ago, the Earl of Essex laid down pipes for the application of the sewage of Watford, by pumping and hose and jet, to about 210 acres of mixed arable and grass land. The results which his Lordship obtained on the application of only 134 tons of sewage per acre to wheat have frequently been held to be conclusive proof of its applicability in small quantities per acre over large areas, to arable land, and to all crops. But in the evidence given by his Lordship before the Sewage Committee of 1862, he stated, very emphatically, that his great error had been the piping of too much land; that he required 5,000 tons per acre for 10 acres of rye-grass; and that, applying the remainder to 35 acres of meadow, he had none to spare for wheat. In other words, although the abandonment of one acre of rye-grass would set free sewage enough for nearly 40 acres of wheat, if applied only at the rate which yielded the large gross return per ton of sewage so frequently quoted, yet his Lordship's practical experience had led him to prefer the application to the one acre of rye-grass rather than to the nearly 40 acres of wheat. Further, his Lordship gave it as his opinion that sewage would not be profitable to the farmer unless he could have it at from $\frac{1}{2}$ d. to $\frac{3}{4}$ d. per ton.

Referring to the question of the application of sewage to corn crops, it may be stated that, in an experiment made by the Commission at Rugby, with oats, a very high gross money return per ton of sewage was also obtained. The experiment was made in the unusually productive season of 1863, and with sewage of about double the average strength of that of the Metropolis, applied during a period of very dry weather. The results were, therefore, quite exceptional, and cannot be taken as affording any indication of what might be expected from the application of small quantities of sewage to corn crops generally, on different soils, and on the average of seasons. There cannot, indeed, be a doubt, that to obtain a maximum gross value of produce from a given amount of sewage, it should be applied in small quantities per acre, and in dry weather. But sewage is produced in large daily amount at all seasons, and must be disposed of as soon as it is produced. It must, therefore, be applied in winter, when of comparatively little value, as well as in summer, when of more, and it would frequently be quite inapplicable to arable land. Moreover, to obtain an increased gross money return per ton of sewage by using it on a

comprehensive scale for corn and other ordinary rotation crops, would involve the extra cost of main distribution over at least a ten-fold, if not frequently a twenty-fold area, and require the application to a great extent by the expensive means of pipes and hose and jet, instead of by the economical one of open runs.

At Malvern and Tavistock the application of sewage to grass land has now been carried on for some years, but at Worthing it has only very recently been commenced.

From this short review of the experience of practical men who have undertaken the utilization of sewage with a view to profit, it appears that, wherever arrangements have been made for the application of small quantities over large areas, to corn and other rotation crops on arable land, and by means of pipes and hose and jet, the undertaking has either been entirely abandoned, or the area greatly limited, and the application confined almost exclusively to meadow and Italian rye-grass. On the other hand, the undertakings which have been the most successful from the agricultural point of view are those in which the arrangements have been adapted for the almost exclusive application to grass, and the application to other crops is only exceptional.

The practical conclusions deducible from the whole inquiry may be briefly stated as follows :—

1. It is only by a liberal use of water that the refuse matters of large populations can be removed from their dwellings without nuisance and injury to health.

2. That the discharge of town sewage into rivers renders them unfit as a water supply to other towns, is destructive of their fish, causes deposits which injure their channels, gives rise to emanations which are injurious to health, is a great waste of manurial matter, and should not be permitted.

3. That the proper mode of both utilizing and purifying sewage is to apply it to land.

4. That, considering the great dilution of town sewage, its constant daily supply at all seasons, its greater amount in wet weather when the land can least bear, or least requires more water, and the cost of distribution, it is best fitted for application to grass, which alone can receive it the year round. It may, however, be occasionally applied with advantage to other crops within easy reach of the line or area laid down for the continuous application to grass.

5. That, having regard both to urban and rural interests, an application of about 5,000 tons of sewage per acre per annum, to meadow or Italian rye-grass, would probably, in the majority of cases, prove to be the most profitable mode of utilization, though the quantity would have to be reduced, provided experience showed that the water was not sufficiently purified; and it is pretty certain that the farmer would not pay $\frac{3}{4}$ d., and it is even very doubtful whether he could afford to pay $\frac{1}{2}$ d. per ton, the year round, for sewage of the average strength of that of the Metropolis (excluding storm-water) delivered on his land.

6. That the direct result of the general application of town sewage to grass land would be an enormous increase in the production of milk, butter, cheese, and meat; whilst, by the consumption of the grass, a large amount of solid manure, applicable to arable land and to crops generally, would be produced.

7. That the cost or profit to a town of arrangements for the removal and utilization of its sewage must vary very greatly, according to its position, and to the character and levels of the land to be irrigated. Where the sewage can be conveyed by gravitation, and a sufficient tract of suitable land is available, the town may realize a profit; but, under contrary conditions, it may have to submit to a pecuniary sacrifice to secure the necessary sanitary advantages.

XII.—*On a New Method of Forming Organo-metallic Bodies.*

By J. ALFRED WANKLYN, Professor of Chemistry at the London Institution.

EIGHT years ago I showed that sodium attacks zinc-ethyl, precipitating zinc, and forming sodium-ethyl. Having observed similar reactions between zinc-ethyl and the metals potassium, lithium, calcium, and strontium, and having regard to the great facility with which these displacements of metal are effected, I was led to compare them to the well-known electro-chemical precipitation from ordinary metallic solutions, and to regard them as examples of a very general method of producing a number of the organo-metallic bodies.

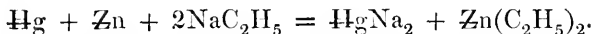
On the present occasion I have to announce a different method of procedure. Instead of taking an organo-metallic compound of

a less positive metal and attacking it with a more positive metal, I take an organo-metallic compound of one of the most positive metals and attack it with mercury, or with an amalgam, or a mixture of mercury with some other metal. The result of the operation is an amalgam of mercury with the positive metal, whilst the organic radical unites either with the mercury or with the other metal.

Thus the new method of forming organo-metallic bodies consists in utilizing for that purpose the great affinity of mercury for the alkali-metals. The following examples will serve to characterize it:—

Mercury, Zinc and Sodium-ethyl.

When the crystalline compound of sodium-ethyl and zinc-ethyl,* which is prepared by treating zinc-ethyl with sodium, is heated in the water-bath with mercury and zinc, it is rapidly resolved into zinc-ethyl and sodium-amalgam, according to the following equation:—



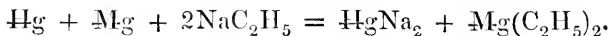
In one experiment, I took about 10 grms. of the compound containing sodium-ethyl, and sealed it up with mercury and zinc, and heated in the water-bath. The result was a quantity of pretty pure zinc-ethyl, not less than 7 grms., and an amalgam of sodium very rich in sodium. I made an analysis of a portion of the 7 grms. of zinc-ethyl. It did not contain so much as 0.5 per cent. of sodium.

Mercury, Magnesium, and Sodium-ethyl.

Some of the crystals containing sodium-ethyl were sealed up with mercury and magnesium-wire. After a short heating in the water-bath they did not form a liquid as in the last case, but a white solid. On opening the tube it was observed that the mercury† was very considerably alloyed with sodium, and that the white solid, which did not fume, took fire spontaneously in the air, and contained magnesium and zinc, but not more than traces of sodium. Evidently, therefore, the reaction was essentially—

* Ann. Ch. Pharm. (1858).

† The mercury effervesced furiously with water, much more violently than a simple amalgam of sodium does. It would seem that the presence of a little metallic magnesium in sodium-amalgam heightens the activity of the amalgam.



the magnesium-ethyl forming a compound with the zinc-ethyl previously in union with the sodium-ethyl.

Mercury, Copper, and Sodium-Ethyl.—Mercury, Iron, and Sodium-Ethyl.—Mercury, Silver, and Sodium-Ethyl.

The result in each of these three cases is mercury-ethyl and sodium-amalgam, the presence of the copper, or iron, or silver appearing to have little or no influence on the course of the reaction.

The foregoing reactions exhibit sodium-ethyl in a new light. It is a sodium compound which possesses the very singular property of giving up its sodium to mercury.

In conclusion, I would remark that since the organo-metallic bodies are liable to be attacked by mercury, very little reliance can be placed on those vapour-density determinations of organo-metallic bodies which have been made by the method of Gay-Lussac, involving, as it does, the employment of mercury in contact with the organo-metallic body in a state of vapour. Most probably the anomalous results obtained by Buckton and Odling, viz., that the vapours of aluminum-methyl and aluminum-ethyl do not expand regularly, depend upon the decomposition of those compounds by the mercury of the bath. And most probably vapour-density determinations of these compounds will be found to yield perfectly intelligible and normal results when the method of Dumas instead of the method of Gay-Lussac is employed.

XIII.—*Chemical Researches on New and Rare Cornish Minerals.*

By A. H. CHURCH, M.A., Professor of Chemistry, R.A. College, Cirencester.

(Continued from vol. III., new series, p. 259.)

IV.—*A New Hydrated Cupric-aluminum Sulphate.*

I HAVE been engaged for some time in analysing certain chrysocollas containing aluminium, similar to the Tuscan specimens

described by Delesse. But no definite composition was presented by these bodies; indeed they were evidently mixtures in most instances. In some of the specimens, I found, as Berthier had previously stated, much sulphuric acid, and at last I have obtained from Mr. Talling some specimens of a mineral almost free from silica and containing over 13 per cent. of sulphuric acid. I noticed it in Mr. Talling's collection, was struck by its appearance, and at once secured a few fragments. The analyses proved satisfactory and accordant, and showed the mineral to be a new and undescribed species. I purpose naming the mineral *Woodwardite* after my valued friend, the late Dr. S. P. Woodward. I shall be glad if this slight act of homage to the memory of an eminent man of science, serve to recall the labours of a paleontologist who was well versed likewise in chemical geology.

Woodwardite occurs in stalactitic forms consisting of minute botryoidal aggregations. It often constitutes a crust about $\frac{1}{5}$ th of an inch in thickness, and possessing the peculiar rippled appearance well seen in some specimens of langite. Woodwardite presents a most striking appearance when viewed with an $1\frac{1}{2}$ inch objective in the microscope, the mammillary or botryoidal aggregations being arranged in irregular columnar masses. No trace of crystalline structure has yet been detected. The mineral is perfectly uniform in appearance, and evidently free, except where in contact with its matrix, from all admixture.

To the unassisted eye, Woodwardite appears nearly opaque, but under the microscope the globules of which it consists are seen to be translucent.

The lustre is between waxy and dull.

The colour of the mineral is a rather greenish turquoise-blue.

The streak and powder are pale blue.

The mineral, though it readily falls to a coarse powder, presents a peculiar toughness and tendency to cohere under the pestle, resembling camphor and sal-ammoniac in this respect.

The hardness is about 2.

The specific gravity is about 2.38. This determination is approximative only; it was made with a specimen freed from interstitial air, but containing a large quantity of hygroscopic or accidental moisture, about 13 per cent. in all probability.

Woodwardite is tasteless and without odour. It dissolves readily in dilute acids, a minute residue, about 1 per cent., of gelatinous silica remaining unaffected.

Heated in a bulb-tube before the blow-pipe, it gives off a large amount of water with a slightly acid reaction, the residue becoming olive-brown, and, finally, black. Heated to 100° the blue tint of the mineral thereby becomes richer.

In vacuo over oil of vitriol woodwardite loses a somewhat variable amount of water. Like many other uncrystallized minerals, it is hygroscopic, and if dried merely between pieces of filtering paper would be found to give a different formula on a dry and on a damp day. One determination of this accidental water gave 13.33 per cent., another a considerably smaller proportion. But the vacuum-dried mineral loses a constant amount of water at 100° ; while the mineral dried at 100° suffers a considerable and perfectly definite further loss at a temperature below redness.

Woodwardite contains traces of phosphoric acid, lime, and magnesia; the percentage of phosphoric acid has been determined, the lime and magnesia do not exist in sufficient quantity to be estimated. The analysis of the mineral offers no difficulty: in one instance (Anal. III) the sample for analysis was thoroughly washed before being employed. The wash waters contained a minute trace of copper.

Analyses I and II were made by my assistant Mr. R. Warrington, Junior.

I. 5.47 grains of the mineral dried in vacuo gave:—

- 06 grain of SiO_2 .
- 21 grain of H_2O at 100° .
- 2.56 grains of CuO .
- 1.00 grain of Al_2O_3 .
- 2.00 grain of BaSO_4 .

II. 10.19 grains dried in vacuo lost at a red heat:—

- 2.41 grains of H_2O ; and gave
- 3.67 grains of BaSO_4 .

III. .4 gramme, dried at 100° , gave:—

- 005 gramme of SiO_2 .
- 073 gramme of H_2O , at a low red heat.
- 191 gramme of CuO .
- 071 gramme of Al_2O_3 .
- 1605 gramme of BaSO_4 .

IV. .5725 gramme dried in vacuo gave :—

- .0035 gramme of SiO_2 .
- .0300 gramme of H_2O at 100° .
- .0955 gramme of H_2O at a low red heat.
- .267 gramme of CuO .
- .099 gramme of Al_2O_3 .
- .209 gramme of BaSO_4 .

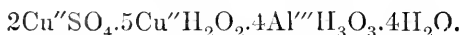
V. .246 gramme dried in vacuo gave :—

- .014 gramme of H_2O at 100° .

VI. .271 gramme dried in vacuo gave :—

- .015 gramme of H_2O at 100° .

The preceding analytical results point without doubt to a definite formula for the mineral, not only after it has become of constant weight in vacuo, but after drying at 100°C . To analyse the mineral, indeed, exactly in its natural condition of moisture would be useless, for as the atmospheric water increases or diminishes so does that of the mineral. But in vacuo over oil of vitriol, Woodwardite acquires in the course of an hour or two a perfect constancy of weight and composition. The formula which suggests itself for the mineral in this state is—

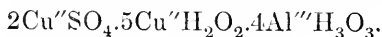


This formula demands the percentages given below :—

		Theory.	Experiment. (mean.)
7 $\text{Cu}''\text{O}$	557.5	46.67	46.87
2 $\text{Al}_2'''\text{O}_3$	206.0	17.27	17.66
2 SO_3	160.0	13.42	12.50
15 H_2O	270.0	22.64	22.86
	<hr/> 1193.5	<hr/> 100.00	<hr/> 99.89

The numbers required by theory agree well with those furnished by experiment, except in the case of the SO_3 in which there is a deficiency of nearly one per cent. in the amount found. This may be accounted for by the occurrence of a small quantity of silicic acid in the mineral.

The formula of the mineral, after it has been dried at 100°C ., is—



This formula demands these percentages—

		Theory.	Experiment. (mean.)
7 CuO	557.5	49.65	48.85
2 Al ₂ O ₃	206.0	18.39	18.33
2 SO ₃	160.0	14.28	13.43
11 H ₂ O	198.0	17.68	18.10
	<hr/>	<hr/>	<hr/>
	1121.5	100.00	98.71

This new mineral, though physically and chemically distinct from Lettsomite, is near that species. Woodwardite is more basic than Lettsomite, both in regard to the cupric and aluminic oxides. The difference is most strikingly seen in the percentage of alumina; in Lettsomite this amounts to 11.06 per cent. only, according to Dr. Percy's analysis: in Woodwardite it is nearly 18 per cent. It is possible to regard the new mineral as a compound of brochantite and gibbsite.

A trace of copper is removed from Woodwardite by digestion in cold water. Analysis IV. was made with a specimen so purified.

The following percentages are those deduced from analyses I., II., IV., V., and VI. Before calculating the results, the small amount of silica found, about 1 per cent., has been subtracted in all the analyses but II. In analysis I. the phosphoric acid, which was found in the alumina, has also been deducted: .03 of a grain of Mg₂'P₂O₇ was obtained, corresponding to .0192 of P₂O₅ :—

Analysis of Woodwardite dried *in vacuo* :—

	I.	II.	IV.	V.	VI.
H ₂ O lost at 100°	3.80	} 23.65	{ 5.28	5.69	5.53
H ₂ O lost on ignition ..	—				
CuO	46.80	—	46.95	—	—
Al ₂ O ₃	17.93	—	17.40	—	—
SO ₃	12.54	12.37	12.60	—	—

The following percentages are based on analyses I., III., and IV., the weights taken being those of the mineral dried till constant at 100° C.

Analyses of Woodwardite dried at 100° C :—

	I.	III.	IV.
H ₂ O lost on ignition. . .	(19.65)	18.48	17.72
CuO	48.67	48.34	49.54
Al ₂ O ₃	18.64	17.97	18.37
SO ₃	13.04	13.95	13.30
	<hr/>	<hr/>	<hr/>
	100.00	98.74	98.93

I have already described to the Society several mineral species new to science as occurring in Cornwall. During my experiments I have obtained numerous results relating to species already described, some of which, however, have not hitherto been recognized as Cornish, or are of rare occurrence.

Melaconite.—This mineral was described by me in March last as occurring in a definite crystallized form. I had then observed forms quite incompatible with the cubical system, and had communicated the fact to Professor Miller of Cambridge: in my notice in the *Chemical News* I stated that it was my intention to measure the crystals, but Professor Maskelyne soon after read a paper on the crystalline form of the mineral before the British Association last summer, and exhausted the subject, although the paper has not yet been published in full. I cannot regret that the crystallographic work has fallen into hands so much more competent to deal with it than my own.

Marmatite.—This black variety of blende occurs in Cornwall. The composition is similar to the Marmato specimen analysed by Boussingault, and is represented by the expression $4\text{ZnS}.\text{FeS}$.

Erinite and Cornwallite.—The only reported locality of erinite is Limerick. But I have a few grains, which I have identified with this species, from Cornwall. I have met more frequently with Cornwallite, a perfectly distinct species. But there exists an impure chrysocolla containing phosphate which has occasionally been mistaken for the latter species.

Autunite.—I have examined a Cornish specimen of autunite incrusting chalcolite, and found it as free from copper as the St. Symphorien specimens.

XIV.—*Action of Nitrous Acid on Naphthylamine.*

By ERNEST T. CHAPMAN.

IN their first paper on this subject,* Messrs. Perkin and Church state that by the action of nitrous acid on naphthylamine, or rather by the action of a soluble nitrite on a salt of naphthylamine, a red base was obtained, having the peculiar property of turning violet on

* Quarterly Journal of Chemical Society, vol. ix, page 1, *et seq.*

the addition of acids, named by them *azo-dinaphthylidiamine*. They state that this substance is analogous to, or identical with, one obtained from dinitronaphthalene by the action of nascent hydrogen; and from an analysis of the former substance they were led to the formula $C_{10}H_8N_2O$. Were this formula correct, the production of the compound in question by the action of nascent hydrogen on dinitronaphthalene would be intelligible; but as they subsequently succeeded in obtaining this compound in a state of purity, and as it was then found to possess the composition $C_{20}H_{15}N_3^*$, it is by no means clear how such a compound could be formed in the manner above stated. And in fact I could not obtain any evidence of the substance by this method, but, on the contrary, obtained a compound of a dark green colour possessing feeble basic properties; it dissolves in alcohol, forming a tolerably bright green solution. Alcohol acidified with hydrochloric acid dissolves much more of it, but with a dirty olive-green colour. Ammonia precipitates it from this solution with its original colour. I could not make the compound crystallise, and have not further examined it.

Messrs. Perkin and Church prepare *azo-dinaphthylidiamine* by acting on 2 eq. of naphthylamine with 1 eq. of nitrous acid, and effect this object by acting on 2 eq. of hydrochlorate of naphthylamine with 1 eq. of nitrite of potash and 1 eq. of potash†—



The process answers admirably; the only points needing attention are that the solution of hydrochlorate of naphthylamine must be cold and dilute.‡

The liquid is at once filled with a white precipitate, which rapidly turns scarlet, and gradually deposits. This is the substance in question; it has only to be filtered off, washed with cold water, and crystallised from alcohol; it is then in a state of perfect purity.

I discovered this substance amongst the products of the action

* Chem. Soc. J. [2] i, 207.

† *Azo-dinaphthylidiamine* is not obtained by acting upon a mixture of 1 eq. of naphthylamine and 1 eq. of hydrochlorate of naphthylamine dissolved in alcohol with 1 eq. of nitrite of potassium. If such a mixture be made, the liquid yields no crystals on evaporation, but a pitch-like substance gradually separates, which dissolves in alcohol with violet colour, turning red on addition of acids. The substance, when quite cold, shows faint signs of crystallisation.

‡ This fact was kindly communicated to me by Prof. Church.

of zinc-ethyl on a mixture of nitro- and dinitro-naphthalene. The observation was accidentally made. I supposed myself to be acting on pure dinitronaphthalene; but on repeating the experiment I could not obtain the same result. As the dinitronaphthalene employed in the first case had only been washed in boiling alcohol and not recrystallised, I supposed that it might contain a small proportion of nitronaphthalene, and that this substance might produce the base in question. As I knew from previous experiments that it was incapable of doing so alone, I concluded that a mixture of the two was necessary to produce the base, and found this conclusion to be borne out by experiment. At the time of making this observation, I was unacquainted with Messrs. Perkin and Church's second paper, and therefore supposed that I had a new substance in hand. Nascent hydrogen, at least in the form of H_2S , will reduce dinitronaphthalene to naphthylamine, $\text{C}_{10}\text{H}_8\text{N}_2\text{O}$, and the same agent will reduce nitronaphthalene to naphthylamine $\text{C}_{10}\text{H}_9\text{N}$. Now if these two substances were to unite, and water were eliminated, $\text{C}_{20}\text{H}_{15}\text{N}_3$ (azo-dinaphthyldiamine), would be produced: $\text{C}_{10}\text{H}_8\text{N}_2\text{O} + \text{C}_{10}\text{H}_9\text{N} = \text{C}_{20}\text{H}_{15}\text{N}_3 + \text{H}_2\text{O}$. And, in fact, on treating a mixture of dinitronaphthalene and nitronaphthalene in alcoholic solution with zinc and hydrochloric acid, the splendid violet colour of azo-dinaphthyldiamine is produced. The colour of course very soon goes, and is not produced for some time after the mixture is made. I intend to examine this reaction more fully.

If, instead of employing in the preparation of azo-dinaphthyldiamine, 1 eq. of nitrous acid to 2 eq. of naphthylamine, we take 1 eq. of each, we still obtain the substance, but in an impure state; and if some of this impure substance be dissolved in alcohol, hydrochloric acid added, and then ether, and the whole diluted with water, the ether will rise to the surface coloured coppery-red, the other portion of the liquid being violet. On separating and evaporating off the ether, a brownish gummy residue remains. On liberating the azo-dinaphthyldiamine by means of ammonia, it will be found that it now readily crystallises from alcohol, which it would not do before this purification. As the gummy substance dissolved by this ether seemed to be formed only when nitrous acid was present in excess, I proceeded to try if I could obtain it by mixing an acidified solution of hydrochlorate of naphthylamine with a solution of nitrite also acidulated; under these circumstances the liquids remained clear, but a slight effervescence took place, the gas liberated being apparently nitrogen; in the course of about ten

minutes the liquid began to get a little thick, and a pitch-like substance gradually separated, gas being evolved during the whole process. If during the earlier stages of this process, the liquid be filtered off and ammonia added, or if before the black substance begins to separate, ammonia be added, azo-dinaphthyldiamine will be precipitated apparently in a state of great purity; at least it crystallises very easily. If instead of employing ammonia, we employ an alcoholic solution of naphthylamine, adding it drop by drop, so long as the white spot formed at first by its addition disappears, we shall arrive at a point at which the addition of a drop of the naphthylamine solution will cause azo-dinaphthyldiamine to separate from the fluid.

Potash and soda produce a reddish-brown precipitate, altogether devoid of basic properties. This substance, if filtered off, washed first with very dilute hydrochloric acid, then with water, and dried at 100° C. forms a chocolate-coloured powder. It is odourless and tasteless, altogether insoluble in water, hot or cold, very slightly soluble in alcohol, slightly more so in ether, but very readily in bisulphide of carbon; benzole also dissolves it pretty freely, but it would not crystallise from any of these liquids. It dissolves in concentrated sulphuric acid with a green colour, but regains its original colour on dilution, and is precipitated apparently unaltered. Concentrated nitric acid also dissolves it, but at the same time alters its composition. The colour of its alcoholic solution is not in the slightest degree affected by acids, and it forms no compounds, so far as I am aware, with acids or bases, or in fact with any class of substances whatsoever. Acted upon by nascent hydrogen it was rapidly decolorised. Heated on the platinum-knife, it melts, gives off a little red fume, and leaves a very difficultly combustible carbonaceous residue; it was analysed by burning it in a stream of common air.

It gave the following numbers—

	Substance.	CO ₂ .	H ₂ O.
Anal. I.	·0535 gave	·1612	and ·0290
„ II. ..	·0914	·2748	·0395
„ III. ..	·1590	·4789	·0708

Or:—

	C.	H.
Anal. I.	82·17 per cent.	and 6·02 per cent.
„ II.	81·99 „ „	4·80 „
„ III.	82·15 „ „	4·95 „

Two nitrogen determinations by Dumas' method gave the following results:—

	Substance.	Nitrogen.	Bar.	Temp.	Nit. p.c.
Anal. I. . .	·495	31·1 c.c.	760	0·	7·88
„ II.. .	·283	18·96 c.c.	760	0·	7·98

From these numbers, excluding the hydrogen in the first analysis, I obtained the following average percentages:—

C.	H.	N.	O. (by diff.)
82·1	4·87	7·93	5·10

but could not obtain a satisfactory formula.

Of course as there is sufficient hydrochloric acid present to saturate both the naphthylamine and the potash of the nitrite, the reaction really takes place on hydrochlorate of naphthylamine, and not on naphthylamine itself. It is possible, therefore, that the nitrous acid effects changes in the naphthylamine-salt, without completely breaking it up, and that it is the addition of the alkali which completes the reaction.

The liquid filtered off after the deposit of the brown substance contained no organic matter.

The black substance before-mentioned as being formed when a solution of hydrochlorate of naphthylamine is allowed to stand with an excess of nitrite of potassium and hydrochloric acid, is, like the brown substance, uncrystallisable, and soluble only with great difficulty in alcohol, ether, or bisulphide of carbon. It forms a yellow solution. It is soluble to a considerable extent in alcoholic ammonia. This solution is brown, and the substance is precipitated from it, apparently unchanged, by the addition of acids. It will not bear a temperature of 100° without undergoing partial decomposition. If heated to a 100° for a considerable time, it partially melts and gives off gas; after this it becomes hard again and is found to have lost about 6 per cent. of its weight. I could obtain no compound with it whatsoever. Its solution is easily decolorised by nascent hydrogen. Sulphurous acid has no effect upon it. Chlorine also seems to be without action, at least in the cold. Sulphuric acid dissolves it without evolution of gas, but it is not re-precipitated in an unchanged form on dilution. Concentrated nitric acid also dissolves it without evolution of gas. It cannot be formed by the action of nitrous

acid on the brown substance. Analysis of the substance furnished the following numbers :—

	Substance.	CO ₂ .	H ₂ O.
Anal. I.	·2305	gave ·522	and ·0615
„ II.	·1225	·2765	·0325

Nitrogen determination :—

Substance taken ·1375 gave 18·5 c. c. of N. at 767 bar. and 15° C.
or :—

Anal. I. gives 61·8 per cent. C. and 3·06 per cent. H.

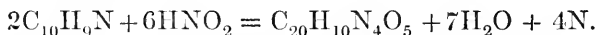
„ II. „ 61·6 „ „ 2·95 „ „

and the nitrogen determination gives 15·84 per cent.

From the foregoing numbers I deduce the following formula,
 $C_{20}H_{10}N_4O_5$.

	Theory.	Found.			Average.
C ₂₀	62·18	61·8	61·6	—	61·70
H ₁₀	2·59	3·06	2·95	—	3·00
N ₄	14·51	—	—	15·84	15·84
O ₅	20·72	—	—	—	19·46 (by dif.)
	<hr/> 100·00				<hr/> 100·00 ³ / ₁

The following equation will show the formation of the substance from naphthylamine :—



Hydriodate of monoethylated naphthylamine, when acted upon by a nitrite, or by nitrous acid, apparently produces the same compounds that a salt of naphthylamine does. At least on dissolving 2 eqs. of the hydriodate in water, and adding 1 eq. nitrite of potash mixed with 1 eq. potash, a base having all the characteristics of azo-dinaphthyldiamine was precipitated. This substance differs totally from monoethylated azo-dinaphthyldiamine, inasmuch as the latter base dissolves with violet colour in alcohol, and is turned crimson by the addition of acids, while the former dissolves with an orange colour, which is turned violet by acids.

XV.—*On Magnesium.*

By J. ALFRED WANKLYN and ERNEST T. CHAPMAN.

THE magnesium met with in commerce appears to be very pure, as is shown by the following determinations of the quantity of hydrogen evolved on dissolving a known weight of the metal in dilute acids. The magnesium ribbon, such as is sold for exhibiting the magnesium-light, was employed, having been first rubbed bright with sand paper.

I.—0.1275 gm. of magnesium ribbon was dissolved in dilute acetic acid, and the hydrogen evolved measured—

Observed volume of gas	127 cub. cent. (moist)
Temperature	11.2° C.
Barometer	754.8 millimetres

Height of water column in the tube containing the gas corresponding to 0.8 millimetres of mercury.

Tension of aqueous vapour at 11.2° C. = 9.8 mm.

Correction of the barometric reading *i. e.* for reduction for temperature = - 1.0 millimetre.

From this we deduce—

Hydrogen = 127 cub. cent. (dry) at 11.2° C. and 743.2 millimetres pressure.

= 119.31 c.c. (dry) at 0° C. and 760 m.m. pressure

= .010665 gm.

(the weight of 1,000 c.c. of hydrogen at normal temperature and pressure being taken at .08939 gm.)

Taking 12 for the equivalent of magnesium, this will correspond to 0.127980 gm. of real magnesium.

Therefore, 100 parts of magnesium-ribbon contain 100.38 parts of real magnesium.

II.—0.1410 gm. of magnesium-ribbon was dissolved in dilute hydrochloric acid, and the hydrogen evolved measured—

Observed volume of gas	141 cub. cent.
Temperature	11.2° C.

Barometer	754·8 mm.
Height of water column in milli- metres of mercury	= 0·8 mm.
Tension of aqueous vapour at 11·2° C.	= 9·8 mm.
Correction of barometer	= 1 mm.

From which we deduce—

$$\begin{aligned}
 \text{Hydrogen} &= 141 \text{ cubic centimeters (dry) at } 11\cdot2^{\circ} \text{ C. and } \\
 &\quad 743\cdot2 \text{ m. m. pressure.} \\
 &= 132\cdot46 \text{ c.c. (dry) at } 0^{\circ} \text{ C. and } 760 \text{ m.m. pres-} \\
 &\quad \text{sure} \\
 &= 0\cdot011841 \text{ gm.}
 \end{aligned}$$

which corresponds to 0·142092 gm. of real magnesium.

Therefore, 100 parts of magnesium-ribbon contain 100·78 parts of real magnesium.

III.—0·1340 gm. of magnesium-ribbon was dissolved in dilute sulphuric acid, and the hydrogen evolved measured—

Observed vol. of gas	133·2 c.c.
Temperature	11° C.
Barometer	754·8 mm.
Height of water column in mercury ..	1·1 mm.
Tension of aqueous vapour at 11° C. ..	9·8 mm.
Correction of barometer	1 mm.

From which we deduce—

$$\begin{aligned}
 \text{Hydrogen} &= 133\cdot2 \text{ c.c. (dry) at } 11^{\circ} \text{ C. and } 742\cdot9 \text{ m.m.} \\
 &\quad \text{pressure} \\
 &= 125\cdot16 \text{ c.c. (dry) at } 0^{\circ} \text{ C. and } 760 \text{ m.m.} \\
 &\quad \text{pressure} \\
 &= 0\cdot011188 \text{ gm.}
 \end{aligned}$$

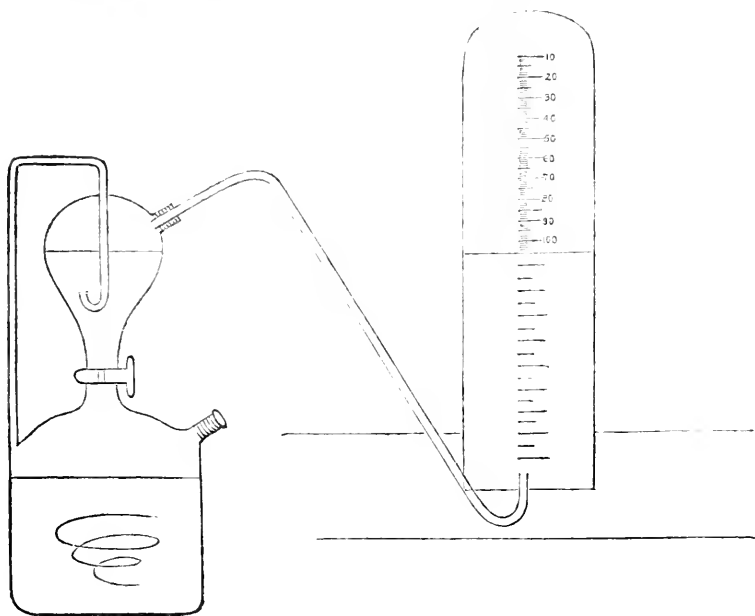
which corresponds to 0·131256 gm. of real magnesium.

Therefore, 100 parts of magnesium-ribbon contain 100·19 parts of real magnesium.

The apparatus employed in these determinations was very simple. A small vessel, such as is made for determinations of carbonic acid, was used for the generation of the hydrogen (see fig.).

The upper part of the vessel contained the dilute acid, the lower portion below the glass stop-cock contained water and the

weighed magnesium-ribbon. The method of using the apparatus, together with the fact that accurate measurements of hydrogen



can be made over water saturated with atmospheric air, will be familiar to those who are conversant with the ordinary processes of gas-analysis. It will, moreover, be obvious that instead of employing the pneumatic trough, as we did, it is quite practicable to use the mercurial trough. We are, however, of opinion that in this particular instance there would be no advantage in doing so.

When it is considered that, next to lithium, the metal which has the lowest equivalent is magnesium, it will be obvious that this determination of the percentage of metallic magnesium from the quantity of hydrogen gas liberated is an extremely rigorous proceeding. Moreover, the determinations may be made with great facility, and are susceptible of a very high degree of precision.

Indeed, this measurement of the hydrogen evolved, when the metal is dissolved in a dilute acid, offers such advantages that we propose to determine equivalents by means of it, believing, that with suitable precautions, it will be found to rival in accuracy the methods hitherto employed.

We have made some observations on the chemical properties of metallic magnesium, which appear to be of interest. Towards the halogens this metal is very indifferent. At ordinary temperatures a solution of iodine in alcohol or ether has very little action on it, and even at 100° C. a solution of iodine in iodide of methyl is only very slowly decolorised by it.

Magnesium may be dipped into liquid bromine without being attacked, and when plunged into chlorine gas it is not immediately tarnished. This inertness of magnesium would seem to be connected with the well-known decomposition of its haloid salts when their aqueous solutions are evaporated to dryness.

With mercury it forms an amalgam endowed with very singular properties. To obtain this amalgam, magnesium is heated with mercury nearly to the boiling point of the latter, whereupon combination takes place, attended with very violent action, somewhat like that between mercury and sodium. An amalgam of magnesium, containing only one part by weight of magnesium to two hundred parts of mercury, tarnishes instantly on exposure to the air, swells up, and becomes very hot when just moistened with water, and decomposes water violently when immersed in it. A comparison was made between sodium-amalgam and magnesium-amalgam. The magnesium-amalgam which has just been described, containing one part of magnesium to two hundred parts of mercury, decomposed water far more rapidly than a sodium-amalgam containing the same proportion, or even twice as much sodium.

It is worthy of note, that whilst amalgamation diminishes the energy of sodium, it increases the energy of magnesium.

The foregoing observations are, for the most part, in accordance with the results obtained by Dr. Phipson, who has shown that iodine may be distilled from magnesium without attacking the metal, and that magnesium alloys with tin, forming with it an alloy capable of decomposing water. It would seem that magnesium has a great tendency to form these alloys capable of decomposing water.

Dr. Phipson's observation that mercury does not amalgamate with magnesium in the cold, depends, most probably, on his not having polished the magnesium. When perfectly clean, magnesium combines slowly with mercury, even in the cold. Dr. Phipson's paper, *Proc. Roy. Soc.* xiii, 217, contains no account of the amalgam of magnesium.

The experiments above described were made in the Laboratory of the London Institution.

XVI.—*A Further Contribution to the History of the Periodides of the Organic Bases.*

By WILLIAM A. TILDEN.

SOME time ago, in a paper which I had the honour of submitting to the Chemical Society, I described several compounds similar to others already known, which result from the union of iodine with the hydriodates of the several organic bases from which they are derived. Since that time I have made a few experiments upon some substances which I have found to possess a similar constitution, containing however chlorine in place of two atoms of the iodine.

These chloriodides have not, perhaps, quite the same interest that attaches to the corresponding iodides, since all that I have examined appear to be destitute of the peculiar action upon light so remarkable in several of those bodies. They are produced simply by adding aqueous protochloride of iodine to an acid aqueous solution in water of the hydrochlorate of any of the bases. A yellow precipitate is obtained, which speedily becomes crystalline. Some few admit of recrystallisation from dilute hydrochloric acid, but the majority, upon attempting resolution, are either entirely broken up, with the formation of products of oxidation, or deposit upon cooling oily substances, with which it was not thought worth while to attempt anything further.

The highly complex natural alkaloids all appear to furnish precipitates of the same nature, which are distinctly crystalline under the microscope; but I thought it would be more satisfactory to examine in detail the compound produced from one of the artificial bases of known constitution.

Chloride of Tetrethylammonium, whose iodide unites with two extra atoms of iodine, producing a teriodide which is crystalline and definite, was dissolved in dilute hydrochloric acid, the solution gently heated, and a quantity of aqueous protochloride of iodine added. Upon standing, large fern-leaf crystals, belonging to the regular system, were deposited.

They were dried in vacuo and analysed.

I. 4837 gramme gave—

•7705 gramme of mixed iodide and chloride of silver Theo-

retically the precipitate should have weighed .7695 gramme.

II. .5347 gramme gave—
 .1612 metallic platinum.

III. .5763 gramme gave—
 .0935 metallic palladium, corresponding to .2228 iodine.

These results give percentages coinciding with those required by the formula $(C_2H_5)_4NCl_2I$.

	Experiment.	Theory.
N	4.264	4.268
I.....	38.66	38.71

This compound is more soluble in dilute hydrochloric acid than in water, which latter causes decomposition. The solution gives reactions precisely resembling those of protochloride of iodine itself. Iodine is liberated from iodide of potassium, proto-salts of iron converted into persalts, and on addition of zinc to the liquid it slowly dissolves, at first precipitating iodine, which after a time disappears. Baryta or lime-water added to the solution drop by drop, likewise causes a liberation of iodine, which subsequently vanishes on adding an excess of the reagent. These changes are sufficient to show that the constitution of this body is represented by the formula I ascribe to it.

Hydrochlorate of triethylamine yields in like manner a compound crystallising in fine needles, but it is so unstable that it could scarcely be obtained in a fit state for analysis. The most easily manageable of these substances I found to be that containing caffeine, which furnishes crystals, apparently oblique rhombic prisms, with the utmost readiness. A quantity of these was dried in vacuo and submitted to analysis.

I. .3797 gramme gave

.5018 gramme of mixed iodide and chloride of silver; by calculation this should have been

.5013 gramme.

II. .7915 dissolved in aqueous iodide of potassium required a quantity of hyposulphite solution, equivalent to .51197 iodine.

Half of this .25598 corresponds to chlorine .0715 gramme.

III. ·7177 gramme gave

·1920 H_2O

·6455 CO_2 .

These numbers agree closely with those required by the formula $(\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H})\text{Cl}_2\text{I}$, as shown below.

	Experiment.	Theory.
C	24·52	24·45
H	2·96	2·79
I	32·20	32·31
Cl	8·99	9·03
Total Cl	—	18·06

Quinine, like the rest, gives a yellow precipitate, which in this case may be obtained in distinct crystals from dilute hydrochloric acid, not however without becoming much darkened in colour. Its solution gives the reactions already described.

These iodides and chloro-iodides naturally appear to be related to the substances formed by the solution of iodine in iodide of potassium, of sodium, and of ammonium, which may fairly be considered as having a similar constitution. Obviously they may all be viewed as constructed either on the type of the triple molecule of hydriodic acid, when the metal would be represented as triatomic:—

Periodide of Potassium.....	$\text{K}''' \text{I}_3$
„ Ammonium	$(\text{NH}_4)''' \text{I}_3$
„ Tetrethylammonium	$\{\text{N}(\text{C}_2\text{H}_5)_4\}''' \text{I}_3$
Chloriodide of „	$\{\text{N}(\text{C}_2\text{H}_5)_4\}''' \text{Cl}_2 \text{I}$
„ Caff-ammonium ..	$\{\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}\}''' \text{Cl}_2 \text{I}$

or they may be considered as derived from the double molecule of hydrochloric or hydriodic acid, in which case they would be written:—

Periodide of Potassium.....	$\text{K}' \text{I}, \text{II}$
„ Ammonium	$\text{NH}_4' \text{I}, \text{II}$
Chloriodide of Tetrethylammonium	$\{(\text{C}_2\text{H}_5)_4\text{N}\} \text{Cl}, \text{ClI}$

XVII.—*On the Estimation of Phosphorus in Iron and Steel.*

By JOHN SPILLER, F.C.S.

IN the course of a somewhat extensive series of analytical examinations which are now being made upon iron and steel, under the direction of the Chemist of the War Department, it has become possible to introduce a modification into the process ordinarily employed in the estimation of phosphorus, whereby a saving of time is effected without impairing the accuracy of the results.

The method of procedure hitherto followed has been that described by Fresenius, in which the nitro-hydrochloric solution of the metal is for the most part reduced to the state of proto-salt by the action of sulphurous acid. The excess of the latter having been expelled by boiling, the solution is cooled, partially neutralized with ammonia, and boiled with acetate of ammonia, whereby all the phosphoric acid is concentrated in the precipitate of basic ferric acetate so formed, whilst the greater portion of the iron remains dissolved as ferrous acetate, and can be separated by filtration. The mixture of phosphate and basic acetate of iron remaining on the filter is then slightly washed, dissolved in hydrochloric acid, and to the warm solution are added successively citric acid, ammonia in excess, and sulphide of ammonium, whereby the iron is precipitated, and may be filtered off, washed perfectly with sulphide of ammonium water, and the solution only reserved. For the extraction of the phosphoric acid, the bulky filtrate is slowly evaporated with full exposure to air, the separated sulphur removed, and the solution precipitated as usual by the mixed chlorides of magnesium and ammonium in the presence of free ammonia. The product is then incinerated and weighed in the form of pyrophosphate of magnesia.

The modification of the process to which reference is now to be made consists in dispensing altogether with the acetic treatment. For the purpose of concentrating the whole of the phosphoric acid contained in the solution of the specimen under examination in a comparatively small proportion of the ferric oxide, it is only necessary to add to the partially reduced and cold solution, aqueous sesqui-carbonate of ammonia, until the precipitate, at first red, assumes a greenish hue—a sign that some of the ferrous carbonate is also thrown down. The whole of the phosphorus is contained

in the precipitate thus obtained, and this fact admits of easy proof, for it is only necessary to add to the filtrate a few drops of ferric chloride, and again the requisite amount of carbonate of ammonia, to procure a further precipitate which can be separately examined. Not only has this been done in several trials, the results of which will presently be described, but the filtrates have been afterwards tested by the acetic process, which has failed to detect any phosphoric acid in the solution. It has, moreover, been found unnecessary to pay particular attention to the thorough expulsion of the excess of sulphurous acid before proceeding to the use of the alkaline carbonate.

A few precautions remain, however, to be noticed; firstly, the *temperature* at which the precipitation (with carbonate of ammonia) should be conducted. The liquid must not be heated above 70°, or at most 75° Fahr., otherwise a loss of phosphate will be experienced, as the following numbers will show:—

Temperature. Deg. Fahr.	Phosphorus, per cent., obtained by	
	1st Pptn.	2nd Pptn.
70	·103	Nil.
100	·146	·004
100	·258	·006
150	·238	·022

The experiment last quoted was an extreme case, both as regards temperature and the presence of sulphurous acid, the excess of which was not boiled off before adding the carbonate.

Secondly, after having dissolved the metallic iron in *red* nitrohydrochloric acid, it is advisable to drop into the flask containing the solution a few small pieces of solid carbonate of ammonia, which, by causing an effervescence in the liquid, will aid in the expulsion of nitrous vapours. The great excess of acid should now be driven off by evaporation, and the diluted solution further neutralized with ammonia, or the carbonate, before adding the bisulphite of ammonia to effect the reduction of the ferric chloride.

The general accordance of the results obtained in experiments made upon several samples of wrought iron taken from the deliveries of three manufacturers will appear from the following tabulated statement:—

Series.	Phosphorus per cent. found.		
I.	·038	·048	·034
II.	·115	·110	·108
III.	·260	·264	·273

And, finally the results obtained in the analysis of *identical* samples of wrought-iron by the carbonate (α), and by the acetate method (β), are shown in two columns as under.

	Phosphorus, per cent.	
	α .	β .
A.	·034	·036
B.	·048	·043
C.	·103	·108*
D.	{ ·142	—
	{ ·148	—
E.	·150	·160

The application of the above process to the analysis of steel does not call for any special remark, but when cast-iron containing much silicium is operated upon, it will always be necessary to search for and separate any silica that may be contained in the ultimate product.

XVIII.—*Note on Mercury-ethyl.*

By E. T. CHAPMAN.

BROMIDE of ethyl may be made to yield mercury-ethyl by the action of dilute sodium-amalgam in the presence of acetic ether, just as the iodide yields it. The reaction takes place equally well with both substances.

The compound was recognised by the action of iodine upon it, and also by converting it into zinc-ethyl by digestion with metallic zinc. This is, I believe, the first instance of an organo-metallic compound of an alcohol-radical, being produced from any other source than the iodide.

I failed in obtaining zinc-ethyl by the action of metallic zinc on bromide of ethyl. Nevertheless, bromide of zinc is formed and gas evolved. The presence of mercury greatly facilitates the reaction.

I may also mention that sodium decomposes alcoholic solutions, both of mercury-ethyl and mercury-methyl, liberating mercury. The sodium first floats on the solution, but rapidly becomes amalgamated and sinks to the bottom, evolving much gas during the process, and finally leaving a globule of mercury.

These experiments were made in the Laboratory of the London Institution.

* Mean of two experiments—·104 and ·112.

XIX.—*A Modification of Berthelot's Experiment for the Formation of Acetylene by imperfect combustion.*

By HERBERT MCLEOD.

IN January last* M. Berthelot described an experiment in which he formed acetylene by the combustion, with an insufficient quantity of air, of bodies containing carbon and hydrogen. He found that not only did hydrocarbons produce this result, but that compounds containing oxygen, in addition, such as ether, or chlorine, such as ethylic chloride, gave rise to the formation of considerable quantities of acetylene. An experiment of this kind he describes as follows:—"Let us fill an eprouvette of 300 cubic centimeters' capacity with the gas, or pour into it a few drops of the volatile liquid; and then add a few cubic centimeters of ammoniacal cuprous chloride, inflame the combustible vapour, and incline the eprouvette almost horizontally, causing it to revolve so as to spread the cuprous reagent over the whole interior surface; we see immediately the cuprous acetylide produced. It is generated in contact with the flame, and below, in the form of a characteristic red precipitate.

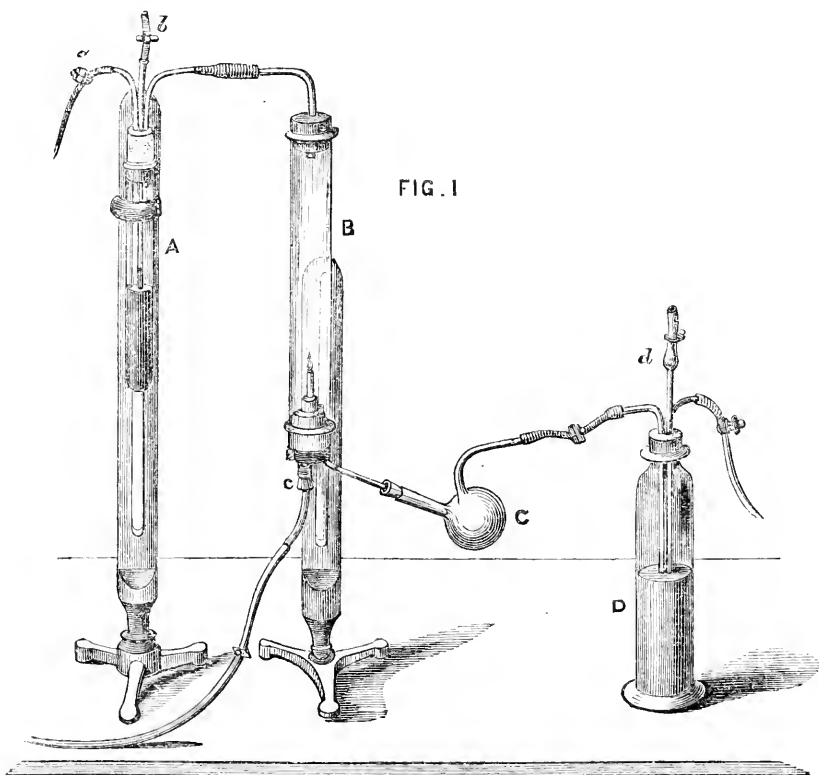
"The experiment is particularly brilliant with ordinary ether and hydride of amyl. It is a beautiful lecture experiment.

"The quantity of acetylene which manifests itself under these circumstances in the form of acetylide is evidently greater than that which is produced under the influence of heat alone acting upon the same compounds. The quantity of acetylene really produced is besides much superior to that which becomes manifest in the form of acetylide, because the greater part of the acetylene burns almost immediately after being formed, and without coming in contact with the reagent. Also, I think, that it will be possible to deduce from this experiment, conveniently modified, a method of preparation of acetylene more advantageous than those which are known up to the present time." It is the object of this communication to describe such a modification.

It is obvious that the most favourable condition for obtaining an imperfect combustion is when the combustion is, so to speak, inverted, and oxygen is made to burn in an excess of the carboniferous gas or vapour. For this purpose an apparatus was em-

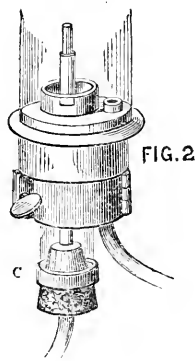
* *Compt. Rend.* lxii, 94.

ployed which had been originally constructed some few years ago for exhibiting the combustion of oxygen in ammonia as an illustration in Dr. Hofmann's course of lectures, and which was used for various similar experiments, such as the combustion of oxygen in hydrogen, of oxygen in coal gas, and of chlorine in hydrogen. The apparatus arranged for the formation of acetylene, is shown in Fig. 1. The experiment is most conclusively performed by burning oxygen in marsh-gas, which is passed from a gas-holder through the tube *a* into a test tube A. When the air has been expelled, a quantity of solution of cuprous chloride



is poured into the test-tube through the tube *b*, and subsequently an excess of ammonia, the tube being then closed by a compression-cock. The presence of any acetylene in the gas would here be indicated by the formation of the characteristic red precipitate. The gas then passes into a vertical cylinder B, closed at the lower

extremity by a perforated cork carrying two tubes, one of which is rather wide; this tube is closed with a conical cork, carrying a piece of quill tube, to the top of which a platinum jet is adapted, by rolling a piece of thin platinum foil into the form of a tube of two or three millimetres in diameter, and placing it within the glass tube, and subsequently fusing the glass in contact with the platinum; the lower extremity of the glass tube is connected with a gas-holder containing oxygen. The arrangement of the lower part of this cylinder is shown in Fig. 2. From the cylinder B the gases pass into a small receiver, and from thence into a bottle D, fitted with a cork and tubes, perfectly similar to the fittings of the test-tube A. When the air has been expelled from the whole apparatus, the solutions of cuprous chloride and ammonia are introduced into D through the tube *d*, which is afterwards closed. To ignite the oxygen in the marsh-gas, the conical cork and jet are removed from the wide tube *c*, a current of oxygen allowed to pass through the jet, the marsh-gas escaping at *c* inflamed, the jet passed through the flame, and the cork rapidly returned to its place. The oxygen then continues burning in the marsh-gas, and in the course of a few seconds, the production of acetylene is indicated by the formation of the red precipitate in the bottle D.



By this process it is easy to obtain from marsh gas about 1·5 grammes of cuprous acetylide in an hour. By employing the gases in larger quantities it will doubtless be possible to increase this amount of product considerably. For the purpose of preparing acetylene, one would, of course, employ ordinary coal gas, perhaps charged with ether vapour, the tube A being dispensed with; and if the oxygen can be replaced by atmospheric air, an experiment which will be tried shortly, the production of this interesting hydrocarbon will become a matter of comparative ease,* and although the gas may not be obtained so rapidly or in such a state of purity as by other methods, yet the simplicity of the process and the ease with which the necessary materials are procured, appear to indicate it as one of the most convenient hitherto suggested. It is quite possible, and even probable, that M. Ber-

* Since writing the above, it has been found possible to replace the oxygen by atmospheric air, and with satisfactory results.

thelot has already modified his experiment in the manner above described, but as far as I am aware no account of it has yet been published.

XX.—*Investigations of the Specific Heat of Solid Bodies.*

By HERMANN KOPP.

(Abstract from the Philosophical Transactions for 1865.)

I. *Historical Introduction.*

1. ABOUT the year 1780 it was distinctly proved that the same weights of different bodies require unequal quantities of heat to raise them through the same temperature, or give out unequal quantities of heat on cooling through the same number of thermometric degrees. It was recognised that for different bodies the unequal quantities of heat, by which the same weights of different bodies are heated through the same range, must be determined as special constants, and considered as characteristic of the individual bodies. This newly discovered property of bodies, Wilke designated as their *specific heat*, while Crawford described it as the *comparative heat*, or as the *capacity* of bodies for heat. I will not enter upon the earliest investigations of Black, Irvine, Crawford, and Wilke, with reference to which it may merely be mentioned that they depend essentially on the thermal action produced when bodies of different temperatures are mixed, and that Irvine appears to have been the first to state definitely and correctly in what manner this thermal action (that is, the temperature resulting from the mixture) depends on the original temperature, the weights, and the specific heats of the bodies used for the mixture. Lavoisier and Laplace soon introduced the use of the ice-calorimeter as a method for determining the specific heat of bodies: and J. T. Mayer showed subsequently that this determination can be based on the observation of the times in which different bodies placed under comparable conditions cool to the same extent by radiation. The knowledge of the specific heats of solid and liquid bodies gained during the last century, and in the first sixteen years of the present one, by these various methods, may be left unmentioned. The individual determinations then made were not sufficiently accurate to be compared with the present ones, nor was any general conclusion drawn with reference to the specific heats of the various bodies.

2. Dulong and Petit's investigations, the publication of which commenced in 1818, brought into the field more accurate deter-

	Berzelius's atomic weights.	Regnault's thermal atomic weights.	Usual equivalent weights.	Modern atomic weights.
Aluminium ..	Al = 13·7	Al = 13·7	Al = 13·7	Al = 27·4
Antimony	Sb = 61	Sb = 61	Sb = 122	Sb = 122
Arsenic	As = 37·5	As = 37·5	As = 75	As = 75
Barium	Ba = 68·5	Ba = 68·5	Ba = 68·5	Ba = 137
Bismuth	Bi = 105	Bi = 105	Bi = 210	Bi = 210
Boron	B = 10·9	B = 10·9	B = 10·9	B = 10·9
Bromine	Br = 40	Br = 40	Br = 80	Br = 80
Cadmium	Cd = 56	Cd = 56	Cd = 56	Cd = 112
Calcium	Ca = 20	Ca = 20	Ca = 20	Ca = 40
Carbon	C = 6	C = 12	C = 6	C = 12
Chlorine	Cl = 17·75	Cl = 17·75	Cl = 35·5	Cl = 35·5
Chromium	Cr = 26·1	Cr = 26·1	Cr = 26·1	Cr = 52·2
Cobalt	Co = 29·4	Co = 29·4	Co = 29·4	Co = 58·8
Copper	Cu = 31·7	Cu = 31·7	Cu = 31·7	Cu = 63·4
Fluorine	Fl = 9·5	Fl = 9·5	Fl = 19	Fl = 19
Gold	Au = 98·5	Au = 98·5	Au = 197	Au = 197
Hydrogen	H = 0·5		H = 1	H = 1
Iodine	I = 63·5	I = 63·5	I = 127	I = 127
Iridium	Ir = 99	Ir = 99	Ir = 99	Ir = 198
Iron	Fe = 28	Fe = 28	Fe = 28	Fe = 56
Lead	Pb = 103·5	Pb = 103·5	Pb = 103·5	Pb = 207
Lithium	Li = 7	Li = 3·5	Li = 7	Li = 7
Magnesium ..	Mg = 12	Mg = 12	Mg = 12	Mg = 24
Manganese ..	Mn = 27·5	Mn = 27·5	Mn = 27·5	Mn = 55
Mercury	Hg = 100	Hg = 100	Hg = 100	Hg = 200
Molybdenum..	Mo = 48	Mo = 48	Mo = 48	Mo = 96
Nickel	Ni = 29·4	Ni = 29·4	Ni = 29·4	Ni = 58·8
Nitrogen	N = 7	N = 7	N = 14	N = 14
Osmium	Os = 99·6	Os = 99·6	Os = 99·6	Os = 199·2
Oxygen	O = 8		O = 8	O = 16
Palladium	Pd = 53·3	Pd = 53·3	Pd = 53·3	Pd = 106·6
Phosphorus ..	P = 15·5	P = 15·5	P = 31	P = 31
Platinum	Pt = 98·7	Pt = 98·7	Pt = 98·7	Pt = 197·4
Potassium	K = 39·1	K = 19·55	K = 39·1	K = 39·1
Rhodium	Rh = 52·2	Rh = 52·2	Rh = 52·2	Rh = 104·4
Rubidium	Rb = 85·4		Rb = 85·4	Rb = 85·4
Selenium	Se = 39·7	Se = 39·7	Se = 39·7	Se = 79·4
Silicium	Si = 21		Si = 14	Si = 28
Silver	Ag = 108	Ag = 54	Ag = 108	Ag = 108
Sodium	Na = 23	Na = 11·5	Na = 23	Na = 23
Strontium	Sr = 43·8	Sr = 43·8	Sr = 43·8	Sr = 87·6
Sulphur	S = 16	S = 16	S = 16	S = 32
Tellurium	Te = 64	Te = 64	Te = 64	Te = 128
Thallium	Tl = 204	Tl = 102	Tl = 204	Tl = 204
Tin	Sn = 59	Sn = 59	Sn = 59	Sn = 118
Titanium	Ti = 25	Ti = 25	Ti = 25	Ti = 50
Tungsten	W = 92	W = 92	W = 92	W = 184
Zinc	Zn = 32·6	Zn = 32·6	Zn = 32·6	Zn = 65·2
Zirconium	Zr = 33·6		Zr = 44·8	Zr = 89·6

minations, and a general law. The investigations of the relations between the specific heats of the elements and their atomic weights date from this time, and were afterwards followed by similar investigations into the relations of the specific heats of compound bodies to their composition. In order to give a general view of the results of these investigations, it is desirable to present, for the elements mentioned in the sequel, a synopsis of the atomic weights assumed at different times, and of certain numbers which stand in the closest connexion with these atomic weights.

For each of the previous columns, the relation of the numbers to each other is alone important, and not the number which is taken as unit or starting-point. Berzelius's atomic weights and Regnault's thermal atomic weights are corrected with the nearest and most trustworthy experimental determinations, without alteration of the bases for the adoption of these numbers. The numerical relations presented in the above Table require, from the chemical point of view, no further explanation. The relations of these numbers to the specific heat form the subject of the investigations which are presented in the sequel.

3. The experiments by which Dulong and Petit* showed, in the case of mercury, various solid metals, and glass, that the specific heat increases with increasing temperature, were made by the method of mixtures. They determined at ordinary temperatures the specific heats of a greater number of elements by the method of cooling.† They found that when the numbers in the first column in § 2 corresponding to the elements Bi, Pb, Au, Pt, Sn, Zn, Cu, Ni, Fe, and S (the Berzelian atomic weights) are multiplied by the respective specific heats of these bodies, approximately the same number is obtained; and that approximately the same number is also obtained when $\frac{1}{2}$ Ag, $\frac{1}{2}$ Te, and $\frac{2}{3}$ Co are multiplied by their corresponding specific heats. They were of opinion that the atomic weights of the elements could and should be so selected that, when multiplied by the specific heats, they should give approximately the same number as product. This observation and this view, which Dulong and Petit stated in 1819 in the following manner, "The atoms of all simple bodies have all exactly the same capacity for heat," have since that time been known as Dulong and Petit's *Law*.

I shall not here dwell upon Potter's investigations on the specific heat of metals and on the validity of Dulong and Petit's

* Ann. Ch. Phys. [2], vii, 142.

† Ibid. x, 395.

law,* but proceed directly to discuss Neumann's investigations, which rank worthily by the side of those of Dulong and Petit.

4. In his "Investigation on the specific heat of Minerals," Neumann (in 1831) first published† more accurate determinations of the specific heats of solid compounds. He investigated a large number of such compounds, especially those occurring in nature, partly by the method of mixture, and partly by the method of cooling; and he determined the sources of error in both these methods, and the corrections necessary to be introduced. In a postscript of this paper, he mentioned that he continued the investigations with an apparatus which, compared with that he had previously used, promised far greater accuracy in the individual results, without needing tedious and troublesome reductions. This apparatus, by means of which the specific heats of solid bodies, which may be heated in a closed space surrounded by steam, can be determined with great accuracy, he has not described.‡

Of the general results of Neumann's investigations, one must be particularly mentioned, that a dimorphous substance has the same specific heat in its two conditions. This he showed was the case with arragonite and calcite, and with iron pyrites and marcasite. But the most important is the discovery that in analogous compounds the products of the atomic weights into the specific heats are approximately equal. Neumann stated this last observation in the following manner:—"In bodies of analogous chemical composition the specific heats are inversely as the stoichiometrical quantities, or, what is the same, stoichiometrical quantities of bodies of analogous chemical composition have the same specific capacity for heat." Neumann adduced 8 carbonates, 4 sulphates, 4 sulphides (MeS), 5 oxides (MeO), and 3 oxides (Me_2O_3), as showing this regularity, which is to be denoted as Neumann's law.§

* Edinburgh Journal of Science, new series, vol. v, p. 75, and vol. vi, p. 166. J. F. W. Johnston's remarks, vol. v, p. 278. I know these papers only from Berzelius's *Jahresbericht*, vol. xii, p. 17, and Gehler's *Physicalisches Wörterbuch*, new edition, vol. x, part 1, p. 805, *et seq.*

† Pogg. Ann. xxiii, 1.

‡ Pape (Pogg. Ann. cxx, 327) has recently described this apparatus. I have had no opportunity of seeing Neumann's memoir cited by Pape, "*Commentatio de emendenda formula per quam calores corporum speciei ex experimentis methodo mixtionis institutis computantur.*" Regiomonti, 1834.

§ The objection of Regnault (*Ann. Ch. Phys.* [3], i, 131) as to the inadequacy of the proofs adduced by Neumann in support of the law are not conclusive.

5. Soon after the publication of Neumann's researches in 1833, Avogadro published* a "Memoir on the Specific Heat of Solid and Liquid Bodies." He there gave a number of determinations of the specific heat of solid bodies made by the method of mixture. As far as can be ascertained by comparison with the most trustworthy of our newer determinations, these results are by no means so accurate as those of Neumann; but they are far more accurate than those which had been obtained up to about 1830, and many of them come very close to the best of our modern results. It would be unjust to Avogadro's determinations† to judge them all by one case, in which he obtained a totally erroneous result (for ice, by a modified method); and by the circumstance that in a subsequent memoir‡ he gives specific heats for several elements, as deduced from his experiments, which are decidedly incorrect.§ Avogadro recognizes the validity of Dulong and Petit's law. With reference to the specific heats of compound bodies, he considers that he had established, with tolerable probability, that for solid and liquid bodies, the same regularity prevails that he had previously deduced for gases from Dulong's experiments. That is, "that the specific heat of the atom of a compound body is equal to the square root of the integral or fractional number expressing the atoms or parts of atoms which go to form the atom of the compound body, such as it exists in the solid or liquid state, taking as unity the specific heat of the atom of a simple body in the same state." He observes that there is a difficulty incidental to the application of this law to solid and liquid bodies, which is not met with in the case of gaseous bodies, in which the composition by atoms or by volumes is held to be directly given by observation. This difficulty consists in knowing what constitution is to be assigned to the body in question for the solid or liquid condition; this constitution, from the conclusions derived from his theoretical considerations, would often be different from that which the body has

* Ann. Ch. Phys. [2] lv. 80, as an abstract from *Memorie della Società Italiana delle Scienze residente in Modena*, t. xx. Fascicolo 3 di fisica.

† They are also found in Gmelin's *Handbuch der Chemie*, 4 Auflage, vol. i. in the Tables, pp. 215-218 *et. seq.* (English Edition I, 241-244 *et. seq.*)

‡ Ann. Ch. Phys. [2] vol. lvii. p. 113.

§ I know Avogadro's investigations only from the abstracts published in the *Annales de Chimie et de Physique*, and am not aware whether the bold corrections of Avogadro urged by Regnault (Ann. Ch. Phys. [2] lxxiii, 10) were used in all his experiments, or only in some.

in the state of gas or vapour. His considerations led him to assume the atomic weights of many elements different from those which Berzelius had given: Avogadro described the atoms, to which the weights assumed by him refer, as *thermal atoms*.

6. R. Hermann published in 1831 a memoir "On the proportions in which Heat unites with the Chemical Elements and their Compounds, and on the Combining Weights considered as quotients of the capacity for Heat of Bodies into their Specific Gravities"*. He gives there a great number of determinations of the specific heat of solid bodies (of a few elements, but chiefly of compound bodies). He made a few experiments in which he used Lavoisier and Laplace's calorimeter†; but by far the greater number of determinations are made by the method of cooling.‡ Many of his results approach very closely to those which are at present considered accurate, but a considerable number among them are decidedly incorrect.

As for Hermann's theoretical results, it must be borne in mind that, regarding matter as he does, not from the point of view of the atomic, but of the dynamical theory, he puts the idea of combination-weights in the place of the idea of atomic weights. The propositions which he endeavours to establish are the following:—The quotients obtained by dividing the specific gravities of the elements§ in the solid state by their specific gravities in the gaseous state, are either equal or stand to each other in simple ratios; they are 1, 2, 15 times as much as a certain base. The same is the case with the products of the specific gravities of the solid elements into their specific heats, that is, with their relative heat; and the number indicating the multiple for a given element is the same for both the above relations. It follows from this that the combining weights m of the elements are proportional to the quotients of their relative heats into their specific gravities in the solid condition; that the products of the specific heats and

* Nouveaux Mémoires de la Société Impériale des Naturalistes de Moscou, vol. iii p. 137.

† Hermann tried to alter this apparatus so as to make it serve for measuring the change of volume which takes place when ice melts; but he did not further follow this application of the modified apparatus.

‡ They are found not quite complete in Gmelin's Handbuch der Chemie, 4 Auflage, in the Tables. pp. 215-218 *et. seq.* (English edition I, 241-244 *et. seq.*)

§ Hermann considers that the specific gravities of the elements in the state of gas or vapour are either obtained by observation, or may be theoretically deduced by assuming that they are in the ratio of the combining weights.

the combining weights for different elements are equal to a constant, and that from the known combining weight of an element its specific heat in the solid form may be calculated (it is equal to $\frac{0.375}{m}$, where m is the combining weight of the substance in question referred to oxygen = 1). For several elements (phosphorus, tellurium, cadmium, and silver for instance) atomic weights are taken which differ from those of Berzelius. In the case of the sulphides, the specific heats may be calculated from those of the constituents, assuming that the specific heats of the elements in these compounds are the same as in the free state. The same holds good for several chlorides and for basic metallic oxides, if the specific heats of chlorine and of oxygen, as given by the above formula, are taken as basis. But in acids a smaller specific heat must be taken for oxygen (one-half in several acids and null in phosphoric acid); and there are even compounds (cassiterite, *e.g.*, or arsenious acid), in which the same element is contained partly with the normal and partly with the modified specific heat*. For oxygen-salts it is to be assumed that both the acid and the base have the same specific heat as in the free state, and hence the specific heat of one constituent (of the acid, for instance) may be calculated, if that of the salt and that of the other constituent (the base) is known; and it is also found that the specific heat of chromic acid in neutral and in acid chromate of lead is the same.

This memoir of Hermann's did not become much known. Unacquainted with it, other philosophers have subsequently developed independently similar opinions.

7. In 1835 Rudberg described a method,† which, by ascertaining the heat developed when salts are dissolved in water, in experiments in which the proportion of the salt to the water was constant, but the temperature of the salt varied, should give a means of at once determining the specific heat of the salt, and of the heat which was either absorbed or became free. Yet the numbers which he obtained from his experiments for the specific heat of solid salts are undoubtedly erroneous.

* Hermann designates such compounds as hermaphrodites. He thinks that an acid and a base may have the same composition, and that they may form salts with each other. Cassiterite, for instance, he considers to be stannate of binoxide of tin.

† Berzelius's *Jahresbericht*, vol. xv, p. 63. Pogg. Ann. xxxv, 474.

Dumas* (in 1838) discussed the possibility of determining the specific heat of organic bodies by the following process. A platinum vessel containing the substance in question, along with a thermometer, is to be heated to 30° or 40° , and then brought into a vessel provided with a second thermometer, and containing water, the temperature being about 5° or 6° lower than that of the surrounding room. When the temperature has risen to the same extent above that of the room, both thermometers are to be observed. I know no determinations made by this method.

8. In 1840 Regnault commenced the publication of a series of important investigations which he had made on specific heat. As they are generally known, I may be more brief in enumerating the contents of the individual publications. In the first which he published, Regnault developed† the reasons which led him to prefer the method of mixture to other processes for determining the specific heats of solid bodies; he described his mode of executing this method, and published the results obtained for a great number of elements. In a second memoir‡ he gave the specific heats of several metallic alloys containing metals in simple atomic ratios, and of a great number of solid chemical compounds; and he published comprehensive experiments on the specific heat of carbon in its different conditions. The investigations announced in the first memoir§ on the specific heat of organic compounds, as well as those promised in the second memoir|| on the specific heat of sulphur at different temperatures, have not to my knowledge been published. But in a third memoir¶ Regnault has investigated the difference in the specific heats of certain metals, according as they are hardened or soft, and also with reference to sulphur according as it is in the native crystallised form, or has solidified a longer or shorter time after being melted; and he has more especially tried to impart greater certainty to the method of cooling. In his subsequent investigations, however, he has used only the method of mixture as being the more certain. These investigations** have given the specific heats of a large number of solid elements, and also of individual compounds.

* Dumas's Thèse sur la question de l'action du calorique sur les corps organiques (Paris, 1838), Ann. Ch. Pharm. xxviii, 151.

† Ann. Ch. Phys. [2] lxxiii, 5.

‡ Ann. Ch. Phys. [3] i, 129.

§ Ibid. [2] lxxiii, 71.

|| Ibid. [3] i, 205.

¶ Ibid. [3] ix, 322.

** Ibid. [3] xxvi, 261 & 268; xxxviii, 129; xlvi, 257; lxiii, 5. Compt. rend. iv, 887.

By his investigations Regnault has removed some objections which seemed to affect Dulong and Petit's law, and has given a great number of new cases in which it applies. He considers* this law to be universally valid, and discusses the reasons why for individual elements the specific heats found do not quite agree with the law, but only approximately. In his view the atomic weight of an element is to be so taken that it agrees with Dulong and Petit's law. He took the atomic weight of silver and of the alkaline metals half as great, and that of carbon twice as great as Berzelius had done. Yet with regard to selecting, by means of the specific heat, from among the numbers which the chemical investigations of an element has given as admissible, that which is the correct one, Regnault does not always express himself decidedly. In the case of carbon† and of silicium‡ he mentions the possibility of their disagreement with Dulong and Petit's law. He proved the validity of Neumann's law for a number of cases very considerably greater than that on which it had originally been based, and he expressed it in a much more general form.§ "In all compounds of analogous atomic composition, and similar chemical constitution, the specific heats are approximately inversely proportional to the atomic weights. Regnault designates the numbers agreeing with this law as thermal atomic weights. He has either determined them directly from the numbers found for the specific heats of the elements in the free state, applying Dulong and Petit's law, or indirectly by ascertaining the specific heat of solid compounds, assuming Neumann's law; or finally (and only in a few cases), he has determined them by means of their probable analogies. These are the atomic weights given in the second column of the table in § 2.

With regard to the relations of the specific heats of solid compounds to those of their constituents, Regnault has shown|| that with metallic alloys, at a considerable distance from their melting points, the specific heats may be calculated from those of their constituents in tolerable accordance with the experimental results, assuming that the specific heats of the metals are the same in the alloys as in the free state. The investigation, whether for true

* Ann. Ch. Phys. [2] lxxiii, 66; further, [3] xxvi, 261, and xlvi, 257.

† Ibid. [2] i, 205. But both before and after (Ibid. [2] lxxiii, 71. and [3] xxvi, 263) Regnault inclined to the view that carbon, with the equivalent=12, and the specific heat found for wood-charcoal, must be considered as obeying Dulong and Petit's law.

‡ Ibid. lxiii, 30.

§ Ibid. i, 199.

|| Ann. Ch. Phys. [3] i, 183.

chemical compounds there is a simple relation between their specific heats and those of their constituent elements, Regnault has reserved* till the conclusion of his experiments on the specific heats of gaseous bodies.† To my knowledge he has published nothing for solid bodies. But in 1862, with reference to the relations which had been recognized between the specific heats and atomic weights of solid, simple, or compound bodies, he spoke as follows.‡ “It is true that these laws, in the case of solid bodies, apply only approximately to simple bodies and those compounds of least complex constitution; for all others it is impossible to pronounce anything in this respect.” From some remarks of Regnault with reference to carbon§ and silicium,|| he considers it possible, or probable, that the specific heat of certain elements in their compounds is different from that which they possess in the free state.

9. In 1840 De la Rive and Marcet published¶ investigations on the specific heat of solid bodies. They made their determinations by the method of cooling. They found that, assuming Berzelius’s atomic weights, selenium, molybdenum, and wolfram fall under Dulong and Petit’s law, which they consider as universally valid; but that carbon forms an exception, and they consider it as probable that its true atomic weight has not yet been ascertained. For several sulphides they found a greater specific heat than was calculated for them, assuming that their constituents have in them the same specific heat as in the free state. They think that for solid as well as for liquid and gaseous compounds, the law governing the specific heat is still unknown. A subsequent memoir by these physicists** treated of the specific heat of carbon in its various conditions.

10. In 1840†† H. Schröder made an investigation as to what volumes are to be assigned to the constituents of solid and liquid compounds when contained in those compounds. In his memoirs on the subject, he expressed the view that the specific heat of compounds depends on the specific heats of the constituents in

* Ibid. p. 132.

† Regnault has made known the results of these experiments in 1853 by a preliminary account in the *Comptes Rendus*, vol. xxxvi, p. 676, and more completely in 1862 in his “*Relation des expériences pour déterminer les lois et les données physiques nécessaires au calcul des machines à feu*,” vol. ii, p. 3.

‡ *Relation, &c.*, vol. ii, p. 289.

§ *Ann. Ch. Phys.* [3] i, 205.

|| Ibid. [3] lxi, 31.

¶ Ibid. [2] lxxv, 113.

** Ibid. [3] ii, 121.

†† *Pogg. Ann.* i, 553.

that particular state of condensation in which they are contained in the compounds in question. In 1841*, reasoning from the results of Regnault's experiments, he endeavoured to show that the atomic heat (that is the product of the atomic weight into the specific heat) of a compound is equal to the sum of the atomic heats for the states of condensation in which the elements are contained in the compound, and to ascertain what atomic heats are to be assigned to certain elements in certain compounds. On the assumption that the atomic heat of metals in compounds is as great as in the free state, he endeavoured to determine the atomic heat of oxygen, sulphur, &c., in certain compounds of these elements with the metals; he came to the conclusion that an element (sulphur for instance) may in some compounds have an atomic heat different from that which it has in the free state; and the same element (sulphur or oxygen for instance) may have different atomic heats in different compounds; but the changes in the atomic heat of an element always ensue in simple ratios. I cannot here adduce the individual results which he obtained when he inferred the atomic heat of an element in a compound by subtracting from the atomic heat of the compound the atomic heat of the other elements in it, which he had calculated either from direct determinations of their specific heat, or from previous considerations. The essential part of Schröder's conception is that in this manner the atomic heat of a body, as a constituent of a compound, may be indirectly determined; and the result is that the atomic heat, at any rate of some elements in compounds, is different from what it is in the free state, and may be different in different compounds, and that the changes are in simple ratios. Schröder considered also that there was probably a connexion between these changes and those of the volumes of the elements, without, however, stating how the one change might be deduced from the other.

11. L. Gmelin (in 1843)† considered it as inadmissible, from the chemical point of view, to assign throughout such atomic weights to the elements as to make them agree with Dulong and Petit's law. Certain exceptions must be admitted. Comparing the specific heats of oxygen, hydrogen, and nitrogen for the gaseous state with the specific heats of other elements in the solid

* Pogg. Ann. lii, 269.

† L. Gmelin's *Handbuch der Chemie*, 4th ed. vol. i, p. 217. (English edition, i, 243.)

state, he came to the conclusion that if the numbers given in § 2 as the equivalents ordinarily assumed be taken as atomic weights, the atomic heat of hydrogen, of nitrogen, and by far the greater number of the elements is equal to about 3·2; several of them twice as great; that of oxygen one-half; that of carbon (as diamond) one-fourth as great. With reference to the dependence of the atomic heats of the compounds on those of the elements, Gmelin expressed the opinion* that in general the elements, on entering into compounds, retain the atomic heats they have in the free state; but for individual elements, especially for oxygen and carbon, it must be assumed that their atomic heat changes in simple ratios with the compounds into which they enter.

12. Wæstyn was also of opinion† that the specific heats of the elements remain unchanged when they enter into chemical compounds. In 1848 he stated as a general proposition: "The quantity of heat necessary to raise the temperature of the atomic weight of a body through 1° is equal to the sum of the quantities of heat necessary to raise the temperature of the atoms, and fractions of atoms, through 1°." If A is the atomic weight and C the specific heat of a compound, $a_1, a_2, a_3 \dots$ the atomic weights‡, and $c_1, c_2, c_3 \dots$ the specific heats of the elements contained in it, and $n_1, n_2, n_3 \dots$ the numbers which express how many atoms of each element are contained in an atom of the compound, then

$$AC = n_1 a_1 c_1 + n_2 a_2 c_2 + n_3 a_3 c_3 \dots$$

As a proof of this law, he compared the calculated values of AC of several compounds (metallic iodides and sulphides) and alloys with the observed values, taking Regnault's determinations of the specific heats of the elements and of the compounds. It follows, further, from that proposition, that if the formula and the values for several compounds are compared with each other, there must be the same differences of the values AC for the same differences of formulæ. Wæstyn showed by a number of examples that this is so approximately. By means of this law, the product of the specific heat and the atomic weight for one constituent of a compound may be found, if this is known for the compound and the other constituents. Wæstyn deduced in this way the product

* Ibid. p. 222: compare an earlier remark of Gmelin which applies to this subject (1840) in the new edition of Gehler's *Physikalisches Wörterbuch*, vol. ix, p. 1941.

† Ann. Ch. Phys. [3] xxiii, 295.

‡ Wæstyn based his considerations on Regnault's thermal atomic weights.

for oxygen (by subtracting from the product for different metallic oxides that found for the metals, and from chlorate of potassium, that for chloride of potassium) to be 2·4 to 2·1 ($O.=8$), and for chlorine 3·0 to 3·5 ($Cl.=17\cdot75$). Wæstyn finally expressed a doubt whether Neumann's law is universally applicable. He laid stress on the circumstance that when two elements gave different products, the difference is also met with in the products for their analogous compounds; and, for instance, the greater products which mercury and bismuth have in comparison with other elements, are also met with in the compounds of these metals.

13. Garnier (in 1852) developed the view*, that not only in the case of elements are the atomic weights A † inversely proportional to the specific heats C , but that the same is the case with water and solid compounds in whose atom n elementary atoms are contained, if the so-called mean atomic weight $\frac{A}{n}$ be compared with the specific heat C ; for elements $A \times C = 3$, and for compound bodies $\frac{A}{n} \times C = 3$ (if $O=8$). He endeavoured to prove this from Regnault's determinations of specific heats. From the latter equation he calculated the specific heat for several compounds. In the case of the basic oxides, sulphides, chlorides, bromides, and iodides, his calculated results agree tolerably with the observed ones; this is less the case with metallic acids and oxygen-salts, for which calculation mostly gives results far too large. Garnier‡ drew, further, from the above proposition, the conclusion that the atomic weight of hydrogen, chlorine, &c., must in fact be taken only half as great as the respective equivalent weights; for only by assuming this smaller atomic weight is the mean atomic weight such that its product with the specific heat is near 3.

In 1852 Bancalari§ repeated that the specific heat of an atom of a compound body (that is, its atomic heat) is equal to the sum of the specific heats of the individual constituent simple atoms, and showed, from a series of examples (oxides, chlorides, sulphates, and nitrates), that, according to that proposition, the

* Compt. Rend. xxxv, 278.

† If Regnault's thermal atomic weights are taken.

‡ Compt. Rend. xxxvii, 130.

§ An abstract from *Memorie della Accademia delle Scienze di Torino* [2], vol. xiii, p. 287, in the *Archives des Sciences Physiques et Naturelles*, vol. xxii, p. 81. I know the contents of this memoir only from this abstract.

atomic heats of many compounds may be calculated in tolerable approximation with those derived from Regnault's experimental investigations, if, for the elements which he investigated, the atomic heats derived from his determinations be taken as a basis, that is, for oxygen ($O=8$) the atomic heat 1.89; for chlorine ($Cl=17.73$) 3.21; for nitrogen ($N=7$) 3.11.

Cannizaro (in 1858 *) has used the proposition, that, in the sense above taken, universally $\frac{AC}{n} = \text{a constant}$, for the purpose of ascertaining the value of n for the atomic weight of different compounds, and therewith ascertaining the atomic weight of elements which are contained in these compounds.

14. Besides those of Regnault, but few experimental determinations of the specific heats of solid bodies have been published. Bede† and Byström‡ have published investigations on the specific heat of several metals at different temperatures§: both sets of experiments were made by the method of mixtures. From the year 1845, Person||, in his investigations on the specific heat of ice, then on the latent heats of fusion, and their relations to the specific heats in the solid and liquid state has determined the specific heat for several solid substances, especially also for some hydrated salts. He worked more especially by the method of mixture. He observed¶, in the case of these salts, that their specific heats may be calculated in close approximation with those found experimentally on the assumption that the constituents, anhydrous salt and water considered as ice, have the same specific

* Il Nuovo Cimento, vol. vii, p. 321. Piazza also gives a statement of this speculation in his pamphlet "Formole atomistiche e tipi chimici," 1863. I know this only from a notice in the Bulletin de la Société Chimique de Paris, 1863.

† An abstract from the Bulletin de l'Académie des Sciences de Belgique, vol. xxii, p. 473, and the Mémoires Couronnés par l'Académie de Belgique, vol. xxvii, appeared in the Bericht über die Fortschritte der Physik im Jahre 1855, dargestellt von der physikalischen Gesellschaft zu Berlin, p. 379.

‡ Abstract from the Oversigt of Stockholm Vetenskaps-Akademien's Förhandlingar, 1860, in the same Jahresbericht, 1860, p. 369.

§ To the experiments of Dulong and Petit on this subject, mentioned in § 3, Pouillet's determinations of the specific heat of platinum at different temperatures must be added (Compt. Rend. ii, 782).

|| Compt. Rend. xx, 1457; xxiii, 162 and 366. Ann. Ch. Phys. [3], xxi, 295; xxiv, 129; xxvii, 250; xxx, 78.

¶ Person expressed this in 1845 (Compt. Rend. xx, 1457), with regard to his determinations of the specific heat of crystallised borax and of ordinary phosphate of soda. He has subsequently published the results of his experiments for the latter salt (Ann. Ch. Phys. [3], xxvii, 253), but I cannot find the number which he found for crystallised borax.

heats in them as in the free state. By the same method, Alluard* (in 1859) determined the specific heat of naphthalene. Schafarik†, lastly, has executed, by the method of mixtures, a series of experiments on the determination of the specific heats of vanadic, molybdic, and arsenious acids.

Quite recently (1863), Pape‡ has published investigations on the specific heat of anhydrous and hydrated sulphates. He worked by the method of mixture, which he modified in the case of salts rich in water, by placing them in turpentine, and observing the increase of temperature produced in the salt and in the liquid by immersing heated copper. As a more general result, Pape finds that for hydrated sulphates of analogous formulæ, the products of the specific heats and the equivalents are approximately equal; and further, that with sulphates containing different quantities of water, the product of the specific heat and the equivalent increases with the quantity of water, in such a manner, that to an increase of each one equivalent there is a corresponding increase in the product.

15. In the preceding paragraphs I have collated, as far as I know them, the investigations on the specific heat of solid bodies, on the relations of this property to the atomic weight, and on the connexion with the chemical composition of a substance. The views which have been expressed relative to the validity of the law of Dulong and Petit§ and that of Neumann, and also as to the question whether the elements enter into chemical compounds with the same specific heats which they have in the free state or with modified ones, are various and often discordant. In this respect it may be difficult to express an opinion which has not been already either stated or hinted at, or which at any rate cannot be naturally deduced from a view previously expressed.

The results to which my investigations on the specific heats of solid bodies have led me are the following:—Each solid substance,

* Ann Ch. Phys [3], lvii 438.

† Berichte der Wiener Akademie der Wissenschaften, xlvii, 248.

‡ Pogg. Ann. cxx, 337 and 579.

§ The universal validity of this law was also defended by Bredow, "On the relation of the Specific Heat to the Chemical Combining Weight." Berlin, 1838. I know this paper only from the mention of it in the new edition of Gehler's "Physiclisches Wörterbuch," vol. x, p. 818. It is also admitted by Mann, in his attempt to deduce this law from the undulatory theory of heat. (1857: Schömilch and Wiltzschel's "Zeitschrift für Mathematik und Physik," II. Jahrgang, p. 280); and by Stefan, in his investigation on the bearing of this law on the mechanical theory of heat (1859: Berichte der Wiener Akademie, vol. xxxvi, p. 85).

at a sufficient distance from its melting-point, has a specific heat, which may vary somewhat with physical conditions (temperature, greater or less density, amorphous or crystalline conditions, &c.); yet the variations are never so great as must be the case if a variation in the specific heat of a body is to be held as a reason for explaining why the determinations of the specific heats of solid elements do not even approximately obey Dulong and Petit's law, nor those of solid compounds of analogous chemical constitution Neumann's law. Neither law is universally valid, although I have found that Neumann's law applies in the case of many compounds of analogous atomic composition, to which, on account of their totally different chemical deportment, different formulas are assigned; and even in cases in which these laws have hitherto been considered as essentially true, the divergences from them are material. Each element has the same specific heat in its solid free state and in its solid compounds. From the specific heats to be assigned to the elements, either directly from experimental determination, or indirectly by calculation on the basis of the law just stated, the specific heats of their compounds may be calculated. I show the applicability of this by a great number of examples.

In reference to this calculation of the specific heats of solid bodies I may here make a remark. The agreement between the results of calculation and experiment is often only approximate; and it is important to bring the approximation closer. On the other hand we may be allowed to ask: What means are there of even approximately predicting and calculating before-hand the specific heat of any inorganic or organic solid compound when nothing but its empirical formula is given? to which among the numbers 0.1, 0.2, 0.3 may it come nearest? Against *this* uncertainty may be set the differences between calculation and observation, exhibited by the numbers in § 103 to 110.

My proof of the propositions given above is based on determinations made by earlier inquirers, and on a not inconsiderable number of my own. I first describe the method by which I worked, and then give the results which I have obtained by its means.

PART II.—*Description of a method of determining the Specific Heat of Solid Bodies.*

16. I have worked by the method of mixture. It is not neces-

sary to discuss the advantages which this method has over that of the ice-calorimeter, at any rate in requiring smaller quantities; nor, as compared with the method of cooling, need I discuss the uncertainties and differences in the results for the same substance, which are incidental to the use of this method, and which Regnault has detailed.*

The method of mixtures has been raised by Neumann and by Regnault to a high degree of perfection. Although by Neumann's method it is possible to determine more accurately the temperature to which the body investigated is heated, Regnault's method allows larger quantities to be used and gives the specific heats of such substances as can be investigated by it as accurately as can at all be expected in the determination of this property. In the case of copper and steel, it is not merely possible to determine their specific heats by its means, but also to say whether and how far there is a difference in the first metal according as it has been heated or hammered, and in the second, according as it is soft or hard. It may be compared with a goniometer, which not only measures the angles of a crystal, but also the differences in the angle produced by heat; or it may be compared to a method for determining the specific gravity of a body, by which not only this property, but also its changes with the temperature may be determined. But along with such methods, simpler ones, though perhaps less accurate, have also their value. Which method is the most convenient or which ought to be used in a given case, depends on the question to be decided by the experiment, or on the extent to which the property in question is constant in the substance examined.

With regard to the relations of the specific heat of solid bodies to their atomic weight and to their composition, Regnault's determinations have shown that both Dulong and Petit's and Neumann's laws are only approximate, and that even the accuracy in determining the specific heat which Regnault attempted, and obtained, could not show that these laws were quite accurate.

Although the description of Regnault's mode of experimenting is so widely known, yet it cannot be said to have become the common property of physicists, or to have found an entrance into the laboratories of chemists, to whom the determination of the specific heat is interesting from its relation to the atomic weight.

* Ann. Ch. Phys. [2] lxxiii, 14; [3] ix, 327.

Very few experiments have been made by this method other than the determinations of Regnault. The method depends on the use of an apparatus which is tolerably complicated and takes up much room. Each experiment requires a long time, and for its performance several persons are required. Regnault has usually worked with very considerable quantities of the solid substance, and in by far the majority of cases at temperatures (usually up to 100°) which many chemical preparations, whose specific heats it is important to know, do not bear. In the sequel I will describe a process, for the performance of which the apparatus can be readily constructed, and for which one operator is sufficient; by which, moreover, the determination of specific heat can be made with small quantities of the solid substance and at a moderate temperature. The method, as I have used it, has by no means the accuracy of that of Regnault; but the results obtained by it are capable of increased accuracy, provided the experiments are executed on a larger scale and within greater ranges of temperature.

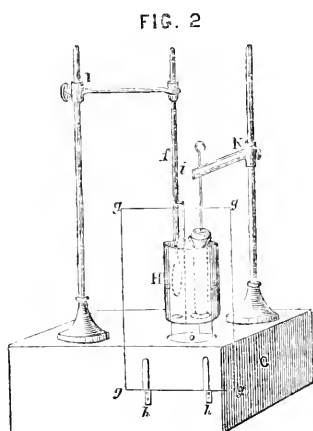
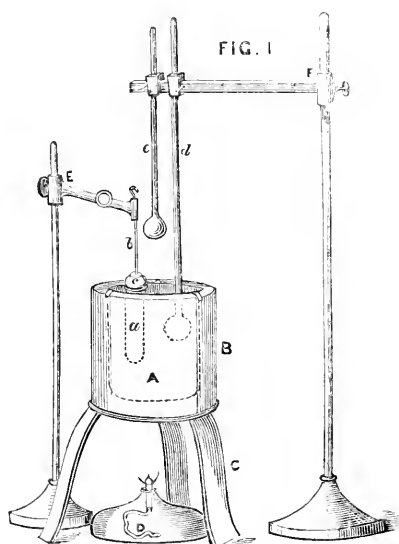
17. The principle which forms the basis of my method is as follows:—To determine the total increase of temperature produced when a glass containing the substance to be investigated, covered by a liquid which does not dissolve it, the whole previously warmed, is immersed in cold water; to subtract from the total increase of temperature that due to the glass and the liquid in it, and to deduce from the difference, which is due to the solid substance, its specific heat.

If, with regard to gain or loss of heat, the glass, in so far as it comes in contact with water, is equivalent to x parts of water, and if f is the weight of the liquid in it, y the specific heat of that liquid, m the weight of the solid substance, M the weight of the water in a calorimeter, including the value in water of the immersed part of a thermometer and of the calorimeter, T the temperature to which the glass and its contents have been heated before immersion in water, and T' the temperature to which the glass sinks when immersed in the water, while the temperature of the latter rises from t to t' , then the specific heat (sp. H.) of the solid substance is

$$\text{sp. H.} = \frac{M(t' - t) - (x + fy) \cdot (T - T')}{m(T - T')}.$$

The glass vessel in which the substance is confined (a in fig. 1) is a tube of glass, the bottom of an ordinary test-tube. In it fits,

but not air-tight, a cork *c*, which is pressed between two small brass plates screwed to a wire *b*. The solid substance to be investigated, in the form of thin cylinders, or in small pieces the size of a pea, along with a liquid of known specific heat, which does not dissolve it, are placed in the tube in such a manner that the liquid covers the solid substance, and that there is a space between the liquid and the cork when it is inserted. The glass, when the cork is fitted, may be suspended to the balance by the wire *b*. Three weighings (1) of the empty glass, (2) after introducing the solid substance, and (3) after introducing the liquid, give the weight of the solid substance (*m*) and of the liquid (*f*).



The heating apparatus (fig. 1) serves to raise the temperature of the glass with its contents. The glass is dipped in a mercury-bath A near its upper edge, and retained by a holder E. The mercury-bath, which consists of a cylindrical glass vessel, is suspended by means of a triangle round the neck of the vessel in an oil-bath B, which stands on a tripod C, and can be heated by a spirit-lamp D. A thermometer *d*,* fixed to the holder F, is also immersed in the mercury-bath.

The flame of the spirit-lamp may be regulated so that the

* The figures are one-sixth of the natural size.

thermometer *d* indicates the same temperature for a long time.* As soon as it may be assumed that the contents of the glass *a* have also risen to this temperature, then, the wire *b* being firmly held in the right-hand by its hook, and the clamp of the holder E in the left, the glass *a* is to be rapidly removed from the heating vessel to the calorimeter H (fig. 2). This is almost the only part of the experiment requiring much practice; the transference of the glass *a* from the one vessel to the other must be effected in an instant, and none of the liquid in the glass must touch the cork.

The calorimeter H stands upon a support G (fig. 2)†, on which there is an oval metal plate *o*. In this there are three depressions, in which fit the three feet of the calorimeter (they are made of very thin hard brass wire). The calorimeter is oval-shaped, and is made of the very thinnest brass plate. In it fits a brass stirrer, made of two parallel plates of equally thin brass, which are joined below by thin wires, and provided with a thin wire ending in a little button *i*, serving as handle. The plates of the stirrer are perforated in such a manner that the glass *a* and a thermometer can be passed through them. Fig. 3 shows more distinctly the construction of the stirrer, also the section of the calorimeter.

For the experiments, the calorimeter is always filled, as nearly as possible, with the same quantity of water. The stirrer is immersed, and a thermometer *f* dipping in the water gives its temperature, which is kept uniform by an upward and downward uniform motion of the stirrer. When the tube *a* is brought into the water of the calorimeter, it is fastened in the clamp of the holder K, which is arranged like the forceps used for biowpipe experiments, so that it stands on the bottom of the calorimeter, and then the stirrer is set to work. This motion of the stirrer, and therewith of the water, must be moderate and uniform in all experiments; this is of some importance for the uniformity and comparability of the experiments. The temperature indicated by

* In order to obtain temperatures constant at about 50°, a spirit-lamp with a thin wick is used, and this is pressed in the sheath so that the alcohol-vapour above it burns with a very small flame. The position of the wick and the intensity of the flame may be conveniently regulated if the upper part of the wick is surrounded by a spiral of thin copper wire whose ends project from the sheath.

† In making the experiment, the actual distance between the calorimeter and the heating apparatus must be greater than is indicated in the figure, but not so great that the glass *a* cannot, by a rapid motion of the arm, be transferred from the mercury-bath to the calorimeter.

the thermometer f rises and soon attains its maximum, which continues for some time, and can be observed with certainty. With this the experiment is concluded. The tube a can be taken from the calorimeter, dried, and used for a new experiment.

The increase of temperature produced in the calorimeter by the tube a and its contents, would be incorrectly given if the warmth of the body of the operator, who moves the stirrer and observes the thermometer, acted on the calorimeter. This is prevented by a glass screen $g\ g\ g\ g$, fig. 2, which is fitted in the brackets $h\ h$, and above which the handle of the stirrer projects.

18. This process for determining the specific heat of solid bodies has the following advantages over those hitherto principally used:—The use of the mercury-bath makes it possible readily to produce, and maintain for any adequate length of time, any temperature desirable in such experiments. The mercury-bath* shares with the air-bath the advantage that nothing which might influence the thermal effect in the calorimeter can adhere to the substance heated in it (in this case the tube and contents), when it is removed. Over the air-bath it has the advantage that any body placed in it takes the temperature of the surrounding medium much more quickly through its entire mass. The communication of heat to the solid substance is materially promoted by the circulation of the liquid in the tube between its particles; the time necessary for the entire contents of the glass to become equally heated is a very short one. Moreover, this very circulation of the liquid between the particles of the solid ensures a quicker and more uniform transmission of the heat of the contents of the glass to the water of the calorimeter; the maximum temperature of this water is soon attained, although the transmission of the excess of temperature must take place through the sides of the glass.

The apparatus just described is very simple. It is readily constructed; the chief point is to have two thermometers which have been compared with each other, one of them (f) graduated in tenths of a degree, while on the other (d) the tenth of a degree can be observed with certainty. The apparatus does not require much space; yet, while the experiment is being made, rapid changes in the temperature of the surrounding air must be avoided.

* In 1848 I already used such a one for heating liquids enclosed in glass tubes, in determining their specific heats (Poggendorff's "Annalen," vol. lxxv, p. 98).

One observer only is required. The experiments which I shall communicate prove that, by means of this apparatus, the specific heat of solid substances, even when only small quantities are taken (in most cases I worked with only a few grammes), may be determined with an accuracy not much less than that attained with larger quantities in more complicated processes.

20. In order to appreciate the trustworthiness of the results arrived at by my mode of experiment, it is important to state with what amount of accuracy the data of observation and the ancillary magnitudes were determined.

For observing the temperature of the water in the calorimeter, I used thermometers made by Geissler, of Bonn, which the kindness of Professor Buff, Director of the Physical Cabinet in Giessen, placed at my disposal. In these thermometers the tube consists of a fine glass thread drawn out at the lamp. The bulb is cylindrical, very thin in the glass, and contains but little mercury. On one (*b*) 1° C. corresponds to a length of almost 5 millims. on the scale, and on the other (*r*) to almost 4.5 millims. Tenths of a degree can be read off directly on the scale, and it is easy to learn to estimate hundredths safely. I have repeatedly compared these two thermometers, between 7° and 24° , with two normal thermometers of my own construction, which agree very well with each other, and on one of which a division corresponds to $0^{\circ}.4878$, and the other to $0^{\circ}.4341$. The differences of the indications between the Geissler's thermometers and these could be considered as constant with those limits; for the differences thus observed all the readings made with the Geissler's thermometers had to be corrected to make them comparable with the indications of the normal thermometer.

The temperature of the mercury-bath was ascertained by means of one of these normal thermometers, and the indications of this thermometer immersed in the bath (*d* in fig. 1.) corrected for the lower temperature of the mercury-thread out of the bath; this latter temperature was given with adequate approximation by the second thermometer, *e*.*

21. The weight of the thin sheet-brass calorimeter, together with stirrer, was 11.145 grms.† Taking the specific heat of brass,

* The paragraphs in this abstract are numbered as in the original memoir.

† At the beginning of these investigations. During their progress the calorimeter was cleaned and dried with bibulous paper a countless number of times, so that its weight diminished by about 0.04 gm. in the course of the experiments. In deter-

according to Regnault, at 0.09391, the calorimetric value in water of this mass of metal is 1.046 gm. Considering that the calorimeter in the experiments was not quite filled with water, but about $\frac{1}{8}$ th remained empty, even after introducing the tube, I put the value in water at 0.872.

In determining the calorimetric water value of the immersed parts of the thermometers, r and b , the following experiments were made. The weight of water in the calorimeter, together with the reduced weight of the metal, was 30.87 grms. When the thermometer r heated to $33^{\circ}.86$ was immersed, the temperature rose from $10^{\circ}.73$ to $10^{\circ}.85$; the immersion of the thermometer b at a temperature of $37^{\circ}.53$ caused a rise from $10^{\circ}.61$ to $10^{\circ}.76$. In both cases the temperature of the water was indicated by means of the other thermometer, the reduced value of which might be neglected under these circumstances. These experiments gave 0.16 as the reduced value of the thermometer r , and 0.17 as the reduced value of the thermometer b . The thermometers have very nearly the same dimensions. Hence I put the reduced value of the calorimeter (that is, of the part of the metal concerned), of the stirrer, and of the immersed part of the thermometer at 1.04 gm. Even if this determination is a few tenths out, it is scarcely appreciable as compared with the quantity of water in the calorimeter. In all following experiments this was between 25.85 and 25.95 grms.

All the subsequent determinations depend on fixing differences of weights and of temperatures. The accuracy of the results depends on the precision with which both kinds of magnitudes are ascertained; and it is useless to determine the weights to $\frac{1}{1000}$ or nearer, if the differences in temperature cannot be determined more accurately than to $\frac{1}{200}$ or $\frac{1}{300}$. I have weighed to centigrammes instead of to milligrammes, by which the time necessary for the weighings is much shortened, and their accuracy not materially lessened.

22. The reduced value x remained to be determined of the glasses (cylindrical tubes of thin glass, see § 17), or, rather, of that part which was immersed in the water of the calorimeter, the quantity of which was always the same. In the following, T is the temperature to which the glass in the mercury-bath was heated (compare fig. 1), M the quantity of water in the calori-

minating the weight of water used in each experiment, the weight which the calorimeter actually had at the time was taken as basis.

meter + the reduced value in water of the other parts of the latter, which required to be taken into account, t the temperature of the water in the calorimeter when the glass was immersed (fig. 2), and τ the temperature to which the water became heated, and which must be considered as that to which the glass cooled.* We have then

$$x = \frac{M(\tau - t)}{T - \tau}.$$

In my experiments I used three glasses, which may be called 1, 2, and 3. To ascertain the reduced value of glass 1, I made the following determinations:—

Temperature of Air 15°·8.

T.	τ .	t .	M. grms.	x .
78·54	17·23	15·72	26·98	0·664
74·38	17·16	15·78	26·97	0·651
75·51	17·14	15·72	26·92	0·655
76·06	17·15	15·73	26·945	0·649
77·32	17·22	15·74	26·96	0·664
Mean..				0·657

A second series of experiments, made in a similar manner, to determine the reduced value for glass 1 gave the following results:—

Temperature of the Air 19°·9–19°·8.

T.	τ .	t .	M. grms.	x .
78·50	21·32	19·93	26·99	0·656
81·86	21·47	20·03	26·98	0·643
80·42	21·43	20·02	26·98	0·645
79·77	21·42	20·03	26·935	0·642
80·14	21·51	20·12	26·955	0·639
Mean..				0·645

The mean of these two means, 0·657 and 0·645, gives as the reduced value in water of glass 1, 0·651 gram.

* If the cork which closes the glass, and by means of the wire passing through it enables it to be handled, is moist, incorrect and discordant values are obtained for it, owing to the evaporation of water in the empty glass so long as this is in the mercury-bath, and to the condensation of aqueous vapour in the glass when it is immersed in the calorimeter.

In like manner, the reduced water-value of glass 2, was found to be 0.487, and that of glass 3 was found to be 0.453.

23. In those experiments in which a glass containing a liquid and perhaps a solid substance is immersed, while warm, in the water of the calorimeter, it may be asked if, when the water has become heated to a certain maximum temperature, the contents of the glass have actually cooled to the same temperature. In earlier experiments made by the method of mixture, it was at once assumed that the temperature assumed by the water of the calorimeter after immersing the solid was actually that also to which the immersed body sank. Neumann has taken into account that the immersed body, when the water shows its maximum temperature, may have a somewhat higher temperature.* Avogadro has also taken this into account,† and Regnault has also allowed for this circumstance in the case in which the mass, immersed in the water of the calorimeter, is a bad conductor of heat.‡ A correction for this fact is certainly inconsiderable and unnecessary if the immersed body conducts heat well, and the range of temperature through which it cools in the liquid is great. This interval of temperature was in my experiments considerably smaller than in those of Neumann and of Regnault; and as in my experiments the excess of heat of the contents of the glass had to pass through its sides to the water of the calorimeter, it might be doubted whether, when the temperature of the water was at its maximum, this temperature could be considered as that of the contents of the glass.

I have endeavoured to answer these questions experimentally. A glass, such as was used for holding the solid investigated and a liquid, was filled with water, and a perforated cork fitted, by means of which the glass could be handled. The glass filled with water was warmed, and then placed in the calorimeter filled with water; a thermometer A, passing through the cork, showed the temperature of the water in the glass; a second, B, showed that of the calorimeter-water. If the glass filled with the warmer water is immersed in the cold water, the following circumstances are observed.§ A sinks very rapidly, while B rises more slowly;

* In the memoirs mentioned in § 4, Pape has also discussed and applied the correction to be made for the above circumstance (Pogg. Ann. cxx, 341).

† Ann. Ch. Phys. [2] lv, 90.

‡ Ibid [2] lxxiii, 26.

§ In these experiments, in order to insure uniformity in the temperature of the water, the stirrer was kept in continual motion, and the same process followed as in ascertaining the specific heat.

if B shows the maximum temperature for the water of the calorimeter (this temperature being called t'), A gives a higher temperature (T') for the contents of the glass. B then slowly sinks and A follows it, while the difference between t' and T' always becomes smaller. In the two following series of experiments, I have endeavoured to determine by how much, under certain conditions, the temperature T' of the water in the glass exceeds the maximum temperature t' of the water in the calorimeter when this maximum temperature as such is observed. I obtained the following results: the temperature of the air in the experiments was $13^{\circ}2$ – $13^{\circ}5$.

Experiments with Glass 1.			Experiments with Glass 2.		
T' .	t' .	Difference.	T' .	t' .	Difference.
15.51	15.13	0.38	15.71	15.50	0.21
14.96	14.72	0.24	15.96	15.65	0.31
16.11	15.94	0.17	15.16	14.91	0.25
15.56	15.36	0.20	14.76	14.47	0.29
14.24	14.05	0.19	14.66	14.33	0.33
15.96	15.64	0.32	15.56	15.24	0.32

A closer agreement in the numbers expressing the difference between T' and t' is difficult to attain, since a certain time is necessary to observe the occurrence of the maximum temperature, and during the time in which the thermometer B remains constant, the thermometer A still sinks; according to the moment at which the maximum temperature is considered to be established, this difference may be obtained different, and the smaller the later the observation is made. Moreover the magnitude of this difference between T' and t' depends on the difference between t' and the temperature of the air. I have always endeavoured to work under the same circumstances, and especially to arrange the experiments so that the maximum temperature of the water in the calorimeter did not exceed by more than 2° the temperature of the air*. For these experiments and the apparatus which I

* A preliminary experiment shows how cool the water in the calorimeter ought to be. Water which is somewhat cooler than the surrounding air may be kept in stock for such experiments by placing it in a cylindrical flask covered externally with filtering paper, and standing in a dish of water, so that the paper is always moist. To warm the water in the calorimeter, it was merely necessary, with apparatus of the dimensions I used, to lay the hand on it for a short time.

used, I assumed, on the basis of the preceding experiments, that if the water of the calorimeter had assumed its maximum temperature t' , the contents of the glass were $0^{\circ}\cdot3$ higher; that is, I put throughout T' , the temperature to which the contents of the glass immersed in the calorimeter had fallen, $=t' + 0^{\circ}\cdot3$.

24. It is a matter of course that, in introducing this correction for obtaining the temperature of the contents of the glass at the time the maximum temperature has been attained in the calorimeter, it is unnecessary to give the indications of T' in hundredths of a degree; and since the temperature T , to which the glass with its contents was heated in the mercury-bath, only serves to deduce the difference $T - T'$, it is unimportant in giving this temperature to do so in hundredths of a degree. The accuracy of the determinations of specific heat, in so far as it depends on determinations of temperature, is limited by the accuracy with which the difference $T - T'$ and $t' - t$ are determined (where t is the original temperature of the water in the calorimeter, and the other letters have the meanings previously assigned to them). To have one of these differences very accurately, while the other is much less accurately determined, avails nothing for the accuracy of the final results. It is at once seen that in my experiments, and especially in those of Neumann and Regnault, the hundredths of a degree have a greater significance for the small difference $t' - t$, than the tenths of a degree for the great difference $T - T'$.

The correction for educing the value of T' , which I have just discussed, is of course more important the smaller the difference $T - T'$; for most of my experiments in which this difference is about 30° , the significance of this correction is inconsiderable, if the contents of the glass be a good conductor. I give a few numbers. The experiments given in § 25 on the specific heat of mercury, which, by using this correction, give it at $0\cdot0335$ in the mean, give it $=0\cdot0331$ if this correction is neglected, that is T' made $=t'$. The fourth series of experiments, given in § 27, for determining the specific heat of coal-tar naphtha A, give it at $0\cdot425$ when this correction is made, and at $0\cdot420$ when it is omitted. The first series of experiments in § 33, for determining the specific heat of sulphur, give it at $0\cdot159$ when this correction is used, and at $0\cdot152$ when it is neglected. Whether in all such cases T' is put $=t'$, or $=t' + 0^{\circ}\cdot3$, is of considerable importance. The correction in question is inadequate if the substance in the

glass is a bad conductor ; for example, when the solid in the glass is a pulverulent or porous mass, in which the moistening liquid stagnates (compare § 18). That, under such circumstances, the numbers obtained for the specific heat are found somewhat too small must be remembered in the case of chromium, and in that of chloride of chromium. Too small numbers are also obtained, if in the experiments the maximum temperature of the cooling water exceeds that of the air by much more than 2° . Such experiments are not comparable with the others, for example, with those made for the purpose of ascertaining the ancillary magnitudes occurring in the calculation of the results ; for them this correction is inadequate, and the loss of heat which the contents of the calorimeter experiences between the time which elapsed between immersing the glass and the establishment of the maximum temperature, is too great.

25. I first attempted to test my method by some experiments in which water or mercury was placed in the calorimeter. For the specific heats of these liquids the following numbers were obtained, calculated by the formula :—

$$\text{sp. H} = \frac{M(t' - t) - x(T - T')}{f(T - T')},$$

in which the signification of f is manifest from what follows, that of the other letters from what has been given before.

In the experiments in which a readily vaporizable liquid was contained in the glass, such as water, or coal-tar naphtha, a sensible formation of vapour took place, although the temperature did not exceed 50° . If the glass containing the liquid was heated in the mercury-bath, vapour was formed in the empty space below the cork which served as stopper ; if the glass was then brought into the water of the calorimeter, this vapour condensed and settled partially on the stopper. The stopper did not act materially on the water of the calorimeter. The quantity of liquid in the glass which acted directly on the water of the calorimeter, decreased somewhat in each experiment ; but this decrease is very inconsiderable. In the following experiments, f denotes first the weight of the liquid in the glass at the commencement of the experiment, and at last its weight at the end of the experiments, that is, after subtracting the liquid which had vaporized and condensed on the stopper. After the end of the experiment the stopper was dried to remove the liquid, and by another weighing

of the glass, together with its contents and stopper, the weight of the liquid still contained in the glass was obtained. The decrease of weight of the liquid in the glass was always found to be inconsiderable, and might without any harm have been neglected; for the last experiment of a series I have always taken the diminished weight of the liquid into account, but for those between the first and the last I have neglected the diminution of the weight of the liquid in the glass. In the following tables, the values of f marked with an asterisk, are those which were formed after drying the stopper.

Two series of experiments in which *water* was contained in the glass, gave the following results for the specific heat of this liquid:—

Experiments with Glass 1. Temperature of the Air $19^{\circ}0$.

T.	T'.	t' .	t .	M.	f .	x .	sp. H.
°	°	°	°	grms.	grms.	grm.	
45.2	20.9	20.62	16.83	26.945	3.43	0.651	1.035
46.6	21.2	20.92	17.03	26.935	„	„	1.013
47.4	21.3	20.96	17.03	26.965	3.42*	„	0.917

Experiments with Glass 3. Temperature of the Air $19^{\circ}0$.

T.	T'.	t' .	t .	M.	f .	x .	sp. H.
°	°	°	°	grms.	grms.	grm.	
46.8	21.1	20.76	17.03	26.95	3.445	0.453	1.004
46.8	21.1	20.83	17.12	26.985	„	„	0.999
47.0	21.2	20.93	17.22	26.935	3.435*	„	0.996

The value found for the specific heat of the contents of the glass comes very near the number 1, assumed for the specific heat of water.

Determinations in which *mercury* was contained in the glass gave the following results for the specific heat of the contents of the glass.

Experiments with Glass 1. Temperature of the Air $13^{\circ}8$ – $14^{\circ}4$.

T.	T'.	t' .	t .	M.	f .	x .	sp. H.
°	°	°	°	grms.	grms.	grm.	
51.1	16.8	16.50	13.41	26.945	53.015	0.651	0.0335
48.5	16.8	16.48	13.64	26.95	„	„	0.0333
45.2	16.5	16.20	13.63	26.965	„	„	0.0333

Experiments with Glass 2. Temperature of the Air $13^{\circ}8$ – $14^{\circ}4$.

T.	T'.	t' .	t .	M.	f .	x .	sp. H.
°	°	°	°	grms.	grms.	grm.	
50.0	17.1	16.79	13.74	26.935	60.015	0.487	0.0335
45.6	16.7	16.41	13.72	26.935	„	„	0.0337

The mean of these five determinations gives 0.0335 for the specific heat of mercury, in accordance with the results found by other observers for this metal (0.0330 between 0° and 100°, Dulong and Petit; 0.0333, Regnault).

26. For the liquid which is to be placed in the glass along with the substance whose specific heat is to be investigated, I could in many cases use water; but many substances, the determination of which is important, dissolve in water, and hence I had to use a different liquid. Coal-tar naphtha has the advantage that it is a mobile liquid, does not dissolve most salts, and does not resinify in contact with the air; but its odour is very disagreeable especially on continuous working, respiring air charged with its vapour appears to act injuriously on the organs of the voice. As compared with water, coal-tar naphtha has the disadvantage, that its specific heat must be specially determined, and any possible uncertainty in this is transferred to the determination of the specific heat of the solid substance; but the thermal action of a given volume of naphtha is only about $\frac{1}{3}$ that of the same volume of water; and in experiments in which the thermal action of a solid substance is determined, along with that of the necessary quantity of liquid which is contained with that substance in a glass, the thermal action due to the solid is a larger fraction of the total if coal-tar naphtha is used than if water is the liquid, which is a favourable circumstance in the accurate determination of specific heat. As it was more especially important to obtain comparability in the results for specific heat, I have, for a great many substances which are insoluble in water, and for whose investigation water might have been used, also employed coal-tar naphtha. Water was used for a few substances which are soluble in coal-tar naphtha (sulphur, phosphorus, sesquichloride of carbon, for instance). Several substances I determined both with water and with naphtha; the results thus obtained agree satisfactorily. To the question as to whether any possible change in the specific heat of naphtha with the temperature can be urged against the use of this liquid, I shall return in a future paragraph.

27. The coal-tar naphtha A which I principally used in the subsequent experiments was prepared from the commercial mixture of hydrocarbons C_nH_{2n-6} , by purifying it with sulphuric acid, treating the portion which distilled between 105° and 120° with chloride of calcium for six days, then again rectifying it, and collecting separately that which passed between 105° and 120°.

This liquid had the specific gravity 0·869 at 15°. Four series of experiments, made to determine its specific heat, gives as a mean result, the number 0·431, between 14° and 52°.

Another sample of coal-tar naphtha, B, used in some of the experiments was found to have a specific heat = 0·419 between 20° and 50°.

29. My experiments were made at very different temperatures. The temperature of the air was often something under 10°, sometimes above 20°. These numbers represent the limits to which the liquid in the glass, together with the solid substance, cooled in the calorimeter. In most experiments I heated the glass with its contents to about 50°, in some cases not so high. Now, for the various intervals of temperature within which the liquid in the glass cooled, can its specific heat be assumed to be always the same? For water this may be done, and for coal-tar naphtha I did not doubt it while engaged in my experiments. I first, when they were finished, became acquainted with Regnault's* investigations on the specific heat of liquids at various temperatures; according to these experiments the specific heat of some liquids considerably increases with the temperature. I have not directly investigated coal-tar naphtha in this respect, but it is probable that the specific heat of this mixture of hydrocarbons $C_n H_{2n-6}$, alters but little with the temperature, and it is certain that this change is without influence on the accuracy of my determinations of the specific heats of solid substances. Regnault's experiments†, made by the method of cooling, show no change for benzole, C_6H_6 , between 20° and 5°, while there is a distinct change in the case of alcohol. For pure benzole‡ I found the specific heat by the method of mixture to be 0·450 between 46° and 19°; Regnault§ found it between 71° and 21° to be 0·436. These numbers, obtained with different preparations, are not indeed comparable for a decision of the question just discussed, but they render improbable a considerable increase in the specific heat of benzole with the temperature. What I more especially lay weight upon is this: the specific heats of solids which I have determined at various temperatures, by their agreement with the

* Relation des expériences . . . pour déterminer les lois et les données physiques nécessaires au calcul des machines à feu, vol. ii, p. 262 (1862).

† Ann. Ch. Phys. [3] ix, 336 and 349.

‡ Pogg. Ann. lxxv, 107.

§ Relation, &c. . . . , ii, 283.

numbers previously found by others, do not indicate any influence of a change of specific heat of naphtha with the temperature.

In the preceding method of experiment, whether water or naphtha of the kind described is contained in the vessel, a temperature much higher than 50° cannot be employed; for otherwise the quantity of liquid evaporating and condensing on the stopper becomes far too considerable. Perhaps with hydrocarbons of higher boiling-points higher temperatures might be ventured upon.

PART III.—*Determination of the Specific Heat of Individual Solid Substances.*

31. By the method whose principle and mode of execution have been discussed in the preceding paragraphs I have determined, the specific heat of a large number of solid substances.* I should have liked to include a still larger number of bodies in my investigations; but a limit was put by the straining of the eyes from constant reading of finely divided scales, and by the injurious action which the long-continued working with coal-tar naphtha produces.

32. The signification of the letters in the statement of the following experiments and their calculation is clear from § 17; in reference to the value of the numbers for M, compare § 21, for x § 22, for T' § 23; y denotes the specific heat of the water or naphtha used in the experiments.

33. *Sulphur*: pieces of transparent (rhombic) crystals from Girgenti. I made three series of experiments with this substance.

I.—Experiments with Water. Glass 1. Temperature of the Air $13^{\circ} \cdot 2$.

T.	T'.	t' .	t .	M.	m .	f .	y .	x .	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
45.8	15.5	15.24	11.74	26.95	4.16	1.765	1.000	0.651	0.163
46.0	16.2	15.93	12.52	26.935	„	„	„	„	0.160
45.2	16.0	15.73	12.42	26.945	„	„	„	„	0.153
45.8	16.4	16.05	12.74	26.96	„	1.75	„	„	0.153
Mean ..									0.159

* We give in this abstract only a few of Professor Kopp's determinations in detail, referring for the rest to the original paper.—Ed.

II.—Experiments with Water. Glass 2. Temperature of the Air 13°.2.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
45.8	16.4	16.07	12.36	26.96	4.815	2.09	1.000	0.487	0.171
47.3	16.6	16.33	12.46	26.95	"	"	"	"	0.170
44.1	16.5	16.15	12.74	26.925	"	"	"	"	0.156
45.1	16.6	16.28	12.77	25.96	"	2.07*	"	"	0.159
Mean ..									0.164

III.—Experiments with Water. Glass 3. Temperature of the Air 17°.2.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
43.7	19.1	18.83	15.79	26.99	4.92	2.065	1.000	0.453	0.166
43.5	19.1	18.84	15.84	26.97	"	"	"	"	0.162
43.3	19.2	18.92	15.92	26.94	"	"	"	"	0.170
43.1	19.2	18.87	15.93	27.98	"	2.05*	"	"	0.166
Mean ..									0.166

Taking the mean of the means obtained in the three series of experiments, 0.159, 0.164, 0.166, we obtain 0.163 as the specific heat of rhombic sulphur between 17° and 45°. By the method of cooling, Dulong and Petit found the specific heat of sulphur at the mean temperature to be 0.188; Neumann found 0.209 by the method of mixture; for sulphur which had been purified by distillation, fused and cast in rolls, Regnault found† the specific heat between 14° and 98° to be 0.2026. In these experiments a development of heat depending on a change from amorphous sulphur into rhombic-crystallised appears to have co-operated, and to have caused the circumstance observed by Regnault, that after immersing the heated sulphur in the water of the calorimeter, the maximum temperature was set up only after an unusually long time. Sulphur which has solidified after being melted, usually contains an admixture of amorphous sulphur—the greater the more the melting point has been exceeded—which, at the ordinary temperature passes slowly, at 100° more rapidly, into crystallised, accompanied by disengagement of heat. The transformation of the sulphur set up by the heating, and continued in the water of the calorimeter, brought about this slow appearance of the maximum temperature, and made the specific heat appear too great;

* After drying the stopper.

† Ann. Ch. Phys. [2] lxxiii, 50.

for Regnault's subsequent determinations,* also made between 97° and 99° and the mean temperature, gave it considerably less; 0.1844 for freshly melted sulphur (in which superfusion had been avoided?); 0.1803 for sulphur which had been melted two months; 0.1764 for what had been melted two years (and which had then given 0.2026); 0.1796 for sulphur of natural occurrence. The difference between the latter result and my own doubtless depends, partially at least, on the fact that Regnault's determination was made between 11° and 99° (the latter of which temperatures is very near the melting point of rhombic sulphur); mine was made between 17° and 45° .†

34. *Boron*.—I have made some experiments with this substance; which have some interest for the question whether this body has essentially different specific heats in its different modifications; but the results are not very trustworthy, owing to the spongy nature of the amorphous boron and the doubtful purity of the crystallised variety.

The *amorphous Boron*‡ which I investigated was pressed in small bars, and had stood several days *in vacuo* over sulphuric acid.

Experiments with Naphtha A. Glass 1. § Temperature of the Air $17^{\circ}.0-17^{\circ}.2$.

T.	T'.	t.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grm.	grms.		grm.	
49.0	18.7	18.73	16.36	26.955	1.52	2.515	0.431	0.651	0.246
48.1	18.6	18.55	16.23	26.965	"	"	"	"	0.254
48.0	18.6	18.64	16.33	26.95	"	"	"	"	0.252
47.9	18.7	18.72	16.42	26.95	"	2.49	"	"	0.262
Mean ..									0.254

Even if the results of the individual experiments agree tolerably with each other they are not very trustworthy; for the quantity of boron (only $1\frac{1}{2}$ grm.) is very small, and the amount of heat due to the boron is a very small part of the total (comp. § 19). Yet I do not consider the result of the above series of experiments (that

* Ann. Ch. Phys. [3] ix, 326 and 344.

† There is nothing known certainly as to whether the different modifications of sulphur have essentially different specific heats. Marchand and Scheerer's experiments on brown and yellow sulphur made by the method of cooling, compare in Journal für Prakt. Chemie, vol. xxiv, p. 153.

‡ "Prepared from boracic acid by sodium, and treated with hydrochloric acid."—Wöhler.

§ See page 177.

|| After drying the stopper.

between 18° and 48° the specific heat of amorphous boron is about 0.254) as very far from the truth. There are no considerable accidental errors of observation in these experiments, to judge from their agreement with one another. Of the constants for calculating the experiments, x and y must be taken into account in regard to any possible uncertainty. It has been assumed that $x=0.615$ and $y=0.431$; if we took $x=0.63$ and $y=0.41$, the specific heat as the mean of four experiments would be $=0.30$; if x were 0.67 and y 0.45 , the specific heat would be 0.21 . But from what has been communicated in § 22 and § 27 in reference to the determination of x and y , it cannot be assumed that any possible uncertainty in reference to these values can reach either of the above limits. It can be assumed with the greater certainty that the specific heat of amorphous boron is between 0.2 and 0.3 and nearly 0.25 , because x and y could not simultaneously both be found too great or too small (if x had been too small y would have been too great, and *vice versa*).

Crystallised Boron.*

Experiments with Naphtha A. Glass 3. Temperature of the Air $18^{\circ} 9-18^{\circ} 7$.

T.	T'.	t' .	t .	M.	m .	f .	y .	x .	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
50.9	20.8	20.52	18.53	26.94	2.82	1.53	0.431	0.453	0.237
51.3	20.8	20.52	18.52	26.975	"	"	"	"	0.233
51.5	20.8	20.53	18.53	26.985	"	"	"	"	0.229
51.4	20.8	20.46	18.43	26.99	"	1.52†	"	"	0.222
Mean ..									0.230

Hence the specific heat of the crystallised (adamantine) boron investigated is 0.230 between 21° and 51° ; it is pretty near that found for amorphous boron, 0.254 . Regnault found $\frac{1}{2}$ (between 98° and 10° and the mean temperature) 0.225 for a specimen of crystallised boron prepared by Rousseau; 0.257 for one prepared by Debray; 0.262 for one obtained from Deville; and 0.235 for a specimen of graphitic boron prepared by Debray. The specific heat of amorphous boron could not be determined by

* "Made in Paris, probably by Rousseau, and doubtless by melting borax with aluminium. To conclude from its external appearance, it probably contained some aluminium and carbon; compare the analysis in Ann. Ch. Pharm. ci. 347.

† After drying the stopper.

‡ Ann. Ch. Phys. [3] lxiii, 31.

Regnault's method, because, when heated to 100° in air, it partially oxidizes into boracic acid, with disengagement of heat (three experiments, in which the quantity of boracic acid formed was determined, and its specific heat, but not the thermal action due to the formation of hydrated boracic acid in immersion in water allowed for, gave respectively 0.405, 0.348, and 0.360, which numbers Regnault does not consider as even approximately representing the specific heat of amorphous boron), and when greatly cooled disengages a quantity of air when immersed in warmer water, which renders the results uncertain.

36. *Carbon*.—It is known how different are the numbers obtained for the specific heat of carbon in its different forms. I have determined the specific heat for comparatively only a few of the modifications of carbon—for gas-carbon, for natural and artificial graphite. Before the experiment, each of these substances was strongly heated for some time in a covered porcelain crucible, and then allowed to cool, and immediately transferred to the glass for its reception, and, after weighing, naphtha was poured over it.

Gas-carbon from a Paris gas-works; very dense, of an iron-grey colour; left very little ash when calcined.* It was used in pieces the size of a pea, and two series of experiments were made.

I.—Experiments with Naphtha A. Glass 1. Temperature of the Air $18^{\circ}9-19^{\circ}2$.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
52.9	20.8	20.53	18.13	26.955	3.135	1.825	0.431	0.651	0.184
52.6	20.9	20.63	18.26	26.98	"	"	"	"	0.185
51.7	20.7	20.42	18.06	26.97	"	"	"	"	0.196
52.4	20.9	20.58	18.23	26.98	"	1.805†	"	"	0.186
Mean ..									0.188

* This carbon, as well as the above-mentioned varieties of graphite, was analyzed in the Laboratory at Giessen by Mr. Huber. The gas-carbon gave, when placed in a platinum boat and burned in a stream of oxygen—

	I.	II.	III.	IV.	V.
Carbon	97.19	98.25	97.73	98.08	98.55
Hydrogen	0.53	0.15	0.68	9.37	1.00
Ash	0.61	0.62	0.73	0.23	0.69
	<u>98.33</u>	<u>99.02</u>	<u>99.14</u>	<u>98.68</u>	<u>100.24</u>

† After drying the stopper.

II.—Experiments with Naphtha A. Glass 3. Temperature of the Air 20°·5—20°·8.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
52·6	22·6	22·33	20·23	26·985	3·345	1·935	0·431	0·453	0·180
52·2	22·5	22·23	20·14	26·985	"	"	"	"	0·183
52·3	22·5	22·20	20·12	26·965	"	"	"	"	0·179
52·5	22·6	22·31	20·22	26·955	"	1·91*	"	"	0·182
Mean ..									0·181

These determinations give, as the average of means of both sets of experiments, the number 0·185 as the specific heat of gas-carbon between 22° and 52°.

Natural graphite from Ceylon. Left very small quantities of ash when calcined.†

I.—Experiments with Naphtha A. Glass 3. Temperature of the Air 18°·9—19°·2.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
51·4	20·8	20·48	18·13	26·975	4·025	2·085	0·431	0·453	0·179
51·4	20·8	20·51	18·13	26·99	"	"	"	"	0·186
51·8	20·8	20·54	18·15	26·975	"	"	"	"	0·181
52·0	20·8	20·54	18·13	26·99	"	2·06*	"	"	0·183
Mean ..									0·183

II.—Experiments with Naphtha A. Glass 1. Temperature of the Air 19°·0—18°·7.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
53·9	21·1	20·77	18·22	26·97	3·515	1·935	0·431	0·651	0·174
52·2	21·0	20·73	18·31	26·96	"	"	"	"	0·176
52·1	21·2	20·86	18·52	26·94	"	"	"	"	0·158
53·0	21·0	20·73	18·32	26·97	"	"	"	"	0·155
52·8	21·0	20·73	18·33	26·965	"	1·91*	"	"	0·160
Mean ..									0·165

* After drying the stopper.

† In Mr. Huber's analyses this substance was placed in a platinum boat, then burned in a porcelain tube in oxygen.

	I.	II.	III.
Carbon	99·11	98·52
Hydrogen	0·17	0·06
Ash	0·26	0·27	0·51
		<u>99·55</u>	<u>99·09</u>

The residual porous ash left after the combustion was tolerably white, with admixed red particles.

III.—Experiments with Naphtha A. Glass 3. Temperature of the Air 19°·9—26°·0.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grms.		gram.	
51·6	21·9	21·55	19·33	26·97	3·90	2·05	0·431	0·453	0·174
51·3	22·0	21·71	19·52	26·955	„	„	„	„	0·174
51·5	22·0	21·70	19·52	26·97	„	„	„	„	0·168
51·5	21·9	21·63	19·42	26·96	„	2·04*	„	„	0·175
Mean ..									0·173

The average of the means of these three series of determinations, 0·183, 0·165, and 0·173, gives 0·174 as the specific heat of Ceylon graphite between 21° and 52°.

Iron graphite from Oberhammer, near Sayn, separated upon black ordnance iron. Thin, very lustrous laminæ, freed from iron by treatment with aqua regia as much as possible, yet not completely.†

I.—Experiments with Naphtha A. Glass 3. Temperature of the Air 19°·0—18°·7.

° .	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
	°	°	°	grms.	grms.	grms.		gram.	
52·5	20·8	20·53	18·21	26·955	2·51	2·445	0·431	0·453	0·186
52·9	21·1	20·84	18·54	26·98	„	2·565‡	„	„	0·156
51·4	20·9	20·64	18·43	26·94	„	„	„	„	0·157
52·0	20·9	20·60	18·33	26·99	„	2·545*	„	„	0·168
Mean ..									0·167

* After drying the stopper.

† This iron graphite, according to Mr. Huber's analyses, in which it was also burned in oxygen in a platinum boat placed in a porcelain tube, gave the following results :—

	I.	II.	III.
Carbon	97·01	96·12	96·37
Hydrogen	0·12	0·18
Ash	4·88	4·87	3·99
	<hr/> 101·89	<hr/> 101·11	<hr/> 100·54

It is probable that both in this graphite and in that of natural occurrence, the hydrogen is not essential, but arises from hygroscopic moisture. The residual ash contained porous particles consisting of sesquioxide of iron and silica, and also small pellets, covered externally with a layer of magnetic oxide of iron: these dissolved in hydrochloric acid, at first quietly, and afterwards with disengagement of hydrogen; and in the solution small blisters of graphite could be perceived. It is owing to the oxidation of the iron that the sum of the constituents in all cases exceeds 100.

‡ After some more naphtha had been added.

II.—Experiments with Naphtha A. Glass 1. Temperature of the Air $19^{\circ}\cdot 9$ — $20^{\circ}\cdot 0$.

T.	T'.	<i>t</i> .	<i>t</i> .	M.	<i>m</i> .	<i>f</i> .	<i>y</i> .	<i>x</i> .	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
52·1	21·9	21·57	19·32	26·94	2·48	2·205	0·431	0·651	0·164
51·7	22·0	21·66	19·45	26·97	"	"	"	"	0·163
51·5	22·0	21·73	19·54	26·98	"	"	"	"	0·162
51·5	22·0	21·66	19·46	26·945	"	2·19*	"	"	0·167
Mean ..									0·164

The average of the means of both these series of experiments, 0·167 and 0·164, gives, as the specific heat of iron graphite between 22° and 52° , the number 0·166.

The results previously known with reference to the specific heat of carbon differ greatly for its different conditions, as also do the results obtained by different inquirers and by different methods for the same condition. But even leaving out of consideration the numbers obtained by De la Rive and Marcet by the method of cooling, there are still considerable differences between Regnault's results, obtained by the method of mixture, and my own. Regnault found, for animal charcoal 0·261, for wood-charcoal 0·241, for gas-carbon 0·209, for natural graphite 0·202, for iron graphite 0·197, for diamond 0·1169; his experiments gave greater numbers for the same substance than my own. I think that, exactly for a substance like carbon in its less dense modifications, my method promises more accurate results than that of Regnault. Even in mine, the substance, after being strongly heated before the experiment, might absorb gases or aqueous vapour, which would make the specific heat too great. But in Regnault's method, this source of error might also operate, and more especially also the source of error due to the disengagement of heat when porous substances are moistened by water. These sources of error, which affect the determination of the specific heat of the various modifications of carbon and make it too high, have the more influence the looser and the more porous the substance investigated. I believe that the only certain determination of the specific heat of carbon is that of diamond, and all other determinations are too high, owing to various circumstances, and in Regnault's experiments with wood and animal charcoal, &c., to the heat disengaged when these substances are moistened by water.

* After drying the stopper.

37. *Silicium*.—I have investigated this substance in four different modifications.

*Amorphous Silicium**.—For the experiments, picked coherent pieces were used, which had stood for several days *in vacuo* over sulphuric acid.

Experiments with Naphtha A. Glass 3. Temperature of the Air $19^{\circ}\cdot 2$.

T.	T'.	<i>t</i> .	<i>t</i> .	M.	<i>m</i> .	<i>f</i> .	<i>y</i> .	<i>x</i> .	sp. H.
°	°	°	°	grms.	grm.	grms.		grm.	
51·5	20·7	20·38	18·13	26·95	1·095	2·88	0·431	0·453	0·251
50·0	20·8	20·54	18·46	26·975	"	"	"	"	0·208
50·4	21·0	20·66	18·55	26·98	"	"	"	"	0·221
50·5	20·9	20·59	18·52	26·935	"	2·87†	"	"	0·177
Mean ..									0·214

The very discordant results of these experiments are very little trustworthy; the quantity of silicium, 1 grm., was too small, and its thermal action inconsiderable as compared with that of the other substances immersed with it in the water of the calorimeter.

Graphitoid Silicium.‡

Experiments with Naphtha A. Glass 3. Temperature of the Air $16^{\circ}\cdot 7$ — $17^{\circ}\cdot 2$.

T.	T'.	<i>t</i> .	<i>t</i> .	M.	<i>m</i> .	<i>f</i> .	<i>y</i> .	<i>x</i> .	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
51·0	18·8	18·51	16·34	26·965	3·155	1·83	0·431	0·453	0·182
52·3	19·1	18·82	16·59	26·975	"	"	"	"	0·181
51·1	18·9	18·62	16·44	26·98	"	"	"	"	0·185
50·4	18·8	18·52	16·43	26·95	"	1·81†	"	"	0·174
Mean ..									0·181

Crystallised Silicium.—Grey needles.§

* "Prepared from silicofluoride of potassium by means of sodium."—Wöhler.

† After drying the stopper.

‡ "Obtained by melting silicofluoride of potassium, or sodium, with aluminium; the aluminium was then extracted with hot hydrochloric acid, and the oxide of silicium with fluoric acid."—Wöhler.

§ "This silicium was prepared from the silicofluoride of potassium, or sodium, by sodium and zinc, and the lead (from the zinc) removed by nitric acid. Whether it was afterwards treated with hydrofluoric acid I cannot say, but probably so. It was quite unchanged when heated in the vapour of hydrochlorate of chloride of silicium (passed by means of hydrogen). Probably it contained, however, like all silicium reduced by zinc, a trace of iron which appears when it is heated in chlorine. An experiment with another portion of such silicium gave, however, so little iron that its quantity could not be determined."—Wöhler.

Experiments with Naphtha A. Glass 1. Temperature of the Air 19°·1.

T.	T'.	t.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
53·8	21·1	20·83	18·53	26·94	2·395	1·955	0·431	0·651	0·168
52·6	21·0	20·74	18·52	26·975	"	"	"	"	0·168
52·3	21·0	20·72	18·52	26·98	"	"	"	"	0·168
51·9	21·0	20·66	18·53	26·975	"	1·935*	"	"	0·156
Mean ..									0·165

Fused Silicium.†

Experiments with Naphtha A. Glass 1. Temperature of the Air 18°·9—18·7.

T.	T'.	t.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
49·0	20·5	20·24	18·40	26·97	4·17	1·555	0·431	0·651	0·142
50·5	20·7	20·43	18·52	26·96	"	"	"	"	0·139
49·7	20·6	20·27	18·42	26·965	"	"	"	"	0·136
50·8	20·7	20·43	18·52	26·94	"	1·145*	"	"	0·136
Mean ..									0·138

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PART IV.—*Table of the Substances whose Specific Heat has been experimentally determined.*

81. The determinations given in the following summary are principally due to Dulong and Petit (D. P.), Neumann (N.), Regnault (R.), and Kopp (Kp.). There are besides some of Person (Pr.), of Alluard (A.), and the recent investigations of Pape (Pp.) are also included. By far the largest number of these determinations have been made by the method of mixture. A few only of the elements investigated by Dulong and Petit, and some of the chemical compounds by Neumann were determined by the method of cooling. Where it is not otherwise stated in reference to the temperature, all determinations refer to temperatures between 0° and 100°. Where the determination has been made beyond these limits, or where a more accurate statement of temperature is important, it is noticed. Where the same substance has been repeatedly investigated by the same observer, the result obtained for the purer preparation, and in general the most certain result, is taken.

* After drying the stopper.

† Wöhler had obtained it from Deville; it formed a cylindrical piece.

In the following tables, the chemical formula is given for each substance (the symbols used both here and subsequently, when not otherwise mentioned, referring to the numbers given in the last column of § 2 as the most recent assumptions for the atomic weights), also the corresponding atomic weight, and the atomic heat, viz., the product of the specific heat and the atomic weight.

82. *Elements and Alloys.*

		Atomic weight.				Specific heat.	Atomic heat.
Ag	..	108	{	0.0557 D. P.	6.02
			{	0.0570 R.	6.16
			{	0.0560 Kp.	6.15
Al	..	27.4	{	0.2143 R.	5.87
			{	0.202 Kp.	5.53
As	..	75	{	0.0814 R.	6.11
Au	..	197	{	0.0298 D. P.	5.88
			{	0.0324 R.	6.38
			{	Amorphous	..	0.254 Kp.	2.77
			{	Graphitoidal	..	0.235 R.	2.56
B	10.9	{	Crystalline	..	0.230 Kp.	2.51
			{	0.225-0.262 R.	2.45-2.86
			{	0.0288 D. P.	6.05
Bi..	..	210	{	0.0308 R.	6.47
			{	0.0305 Kp.	6.41
Br	..	80	{	Between -78° and 20°	..	0.0843 R.	6.74
			{	Wood charcoal	0.241 R.	2.89
			{	Gas carbon	0.204 R.	2.45
			{	0.185 Kp.	2.22
C	12	{	Natural graphite	..	0.202 R.	2.42
			{	0.174 Kp.	2.09
			{	Iron graphite	0.197 R.	2.36
			{	0.166 Kp.	1.99
			{	Diamond	0.1469 R.	1.76
Cd	..	112	{	0.0567 R.	6.35
			{	0.0542 Kp.	6.07
Co	..	58.8	{	0.1067 R.	6.27
			{	0.0949 D. P.	6.02
Cu	..	63.4	{	Hammered	..	0.0935 R.	5.93
			{	Heated	0.0952 R.	6.04
			{	0.0920 Kp.	5.90
			{	0.1100 D. P.	6.16
Fe	..	56	{	0.1138 R.	6.37
			{	0.112 Kp.	6.27
Hg	..	200	{	Between -78° and -40°	..	0.0319 R.	6.38
I	127	{	0.0541 R.	6.87
Ir..	..	198	{	0.0326 R.	6.45
K..	..	39.1	{	Between -78° and ?	0.1655 R.	6.47
Li..	..	7	{	0.9408 R.	6.59
Mg	..	24	{	0.2499 R.	6.00
			{	0.245 Kp.	5.88
Mn	..	55	{	0.1217 R.	6.69
Mo	..	96	{	0.0722 R.	6.93
Na	..	23	{	Between -34° and 7°	..	0.2934 R.	6.75
Ni	..	58.8	{	0.1092 R.	6.42
Os	..	199.2	{	0.0311 R.	6.20

		Atomic weight.				Specific heat.	Atomic heat.
P	31	{	Yellow, between 13° and 36° ..	0.202	Kp.	6.26
			 7° .. 30° ..	0.1895	R.	5.87
			 -21° .. 7° ..	0.1788	Pr.	5.54
			 -78° .. 10° ..	0.1740	R.	5.39
Pb	207	{	Red 15° .. 98° ..	0.1648	R.	5.26
				0.0293	D. P.	6.06
				0.0314	R.	6.50
				0.0315	Kp.	6.52
Pd	106.6	{	0.0593	R.	6.32
				0.0314	D. P.	6.20
				0.0324	R.	6.40
				0.0325	Kp.	6.42
Rh	104.4	{	0.0580	R.	6.06
				0.1880	D. P.	6.02
				0.1776	R.	5.68
				0.163	Kp.	5.22
S	32	{	Rhombic, between 14° and 99°	0.1776	R.	5.68
			 17° .. 45°	0.163	Kp.	5.22
				0.0507	D. P.	6.20
				0.0508	R.	6.20
Sb	122	{	0.0523	Kp.	6.38
				0.0746	R.	5.92
				0.0762	R.	6.05
				0.0745	R.	5.92
Se..	79.4	{	Amorphous, bet. -27° and 8°	0.0746	R.	5.92
				Crystalline, .. 98° .. 20°	0.0762	R.	6.05
			 -18° .. 7°	0.0745	R.	5.92
				0.181	Kp.	5.07
Si..	28	{	Graphitoidal	0.165	Kp.	4.62
				Crystallised	0.167-0.179	R.	4.68-5.01
				Fused	3.86
				0.138	Kp.	3.86
Sn	118	{	0.156-0.175	R.	4. -4.90
				0.0514	D. P.	6.06
				0.0562	R.	6.63
				0.0548	Kp.	6.46
Te	128	{	0.0474	R.	6.07
				0.0475	Kp.	6.08
				0.0336	R.	6.85
				0.0334	R.	6.15
Tl..	204	{	0.0927	D. P.	6.04
				0.0956	R.	6.23
				0.0932	Kp.	6.08
			
W..	184	{
			
			
			
Zn	65.2	{
			
			
			

Alloys which only melt far above 100°.

Bi Sn	328	0.0400	R.	13.1
Bi Sn ₂	446	0.0450	R.	20.1
Bi Sn ₂ Sb	568	0.0462	R.	26.2
Bi Sn ₂ SbZn ₂	698.4	0.0566	R.	39.5
Pb Sb	329	0.0388	R.	12.8
Pb Sn	325	0.0407	R.	13.2
Pb Sn ₂	443	0.0451	R.	20.0

83. Arsenides and Sulphides.

Co As ₂	208.8	Speis-cobalt	0.0920	N.	19.2
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As the locality of this mineral is not given, the formula and atomic weight are not certain. Metals replacing the cobalt can, however, have little influence on the atomic weight and the product.

		Atomic weight.				Specific heat.	Atomic heat.
Ag ₂ S	..	248	Fused	0·0746 R.	18·5
Co As S	..	166	Cobalt-glance	0·1070 N.	17·8
Cu ₂ S	..	158·8	{ Fused	0·1212 R.	19·2
Fe As S	..	163	{ Copper-glance	0·130 Kp.	19·1
As S	..	107	Mispickel	0·1012 N.	16·5
Co S	..	90·8	Commercial	0·1111 N.	11·9
Cu ₁ Fe ₁ S	..	91·7	{ Fused	0·1251 R.	11·4
Fe S	..	88	{ Copper pyrites	0·1289 N.	11·8
Hg S	..	232	{ Fused	0·131 Kp.	12·1
Ni S	..	90·8	{ Cinnabar	0·1357 R.	11·9
Pb S	..	239	{ " "	0·052 N.	12·1
Sn S	..	150	{ " "	0·0512 R.	11·9
Zn S	..	97·2	{ " "	0·0517 Kp.	12·0
Fe ₇ S ₈	..	648	{ Fused	0·1281 R.	11·6
As ₂ S ₃	..	246	{ Galena	0·053 N.	12·7
Bi ₂ S ₃	..	516	{ " "	0·0509 R.	12·2
Sb ₂ S ₃	..	340	{ " "	0·0490 Kp.	11·7
Fe S ₂	..	120	{ Fused	0·0837 R.	12·6
Mo S ₂	..	160	{ Zinc-blende	0·1145 N.	11·1
Sn S ₂	..	182	{ " "	0·1230 R.	12·0
			{ " "	0·120 Kp.	11·7
			{ Magnetic pyrites	0·1533 N.	99·3
			{ " "	0·1602 R.	103·8
			{ Natural	0·1132 N.	27·8
			{ Artificial	0·0600 R.	31·0
			{ Natural	0·0907 N.	30·8
			{ Artificial	0·0840 R.	28·6
			{ Marcasite	0·1332 N.	16·0
			{ Iron pyrites	0·1275 N.	15·3
			{ " "	0·1301 R.	15·6
			{ " "	0·126 Kp.	15·1
			{ Natural	0·1067 N.	17·1
			{ " "	0·1233 R.	19·7
			{ Aurum musivum	0·1193 R.	21·7

84. Chlorine, Bromine, Iodine, and Fluorine Compounds.

Ag Cl	..	143·5	Fused	0·0911 R.	13·1
Cu Cl	..	98·9	"	0·1383 R.	13·7
Hg Cl	..	235·5	Sublimed	0·0521 R.	12·3
K Cl	..	74·6	{ Fused	0·1730 R.	12·9
Li Cl	..	42·5	{ " "	0·171 Kp.	12·8
Na Cl	..	58·5	{ " "	0·2821 R.	12·0
Rb Cl	..	120·9	{ " "	0·2140 R.	12·5
N H ₄ Cl	..	53·5	{ Rock-salt	0·213 Kp.	12·5
Ba Cl ₂	..	208	{ Fused	0·219 Kp.	12·8
Ca Cl ₂	..	111	{ Fused	0·112 Kp.	13·5
HgCl ₂	..	271	{ Crystallised	0·112 Kp.	13·5
MgCl ₂	..	95	{ Fused	0·373 Kp.	20·0
MnCl ₂	..	126	{ " "	0·0896 R.	18·6
Pb Cl ₂	..	278	{ " "	0·0902 Kp.	18·8
Sn Cl ₂	..	189	{ " "	0·1642 R.	18·2
			{ Sublimed	0·0689 R.	18·7
			{ Crystallised	0·0640 Kp.	17·3
			{ Fused	0·1946 R.	18·5
			{ " "	0·191 Kp.	18·2
			{ " "	0·1425 R.	18·0
			{ " "	0·0664 R.	18·5
			{ " "	0·1016 R.	19·2

		Atomic weight.				Specific heat.	Atomic heat.
Sr Cl ₂	..	158.6	Fused	0.1199 R.	19.0
Zn Cl ₂	..	136.2	"	0.1362 R.	18.6
Ba Cl ₂ . 2 H ₂ O	..	244	Crystallised	0.171 Kp.	41.7
Ca Cl ₂ . 6 H ₂ O	..	219	Between -21° and 0°	0.345 Pr.	75.6
Zn K ₂ Cl ₄	285.4	Crystallised	0.152 Kp.	43.4
Pt K ₂ Cl ₆	..	488.6	"	0.113 Kp.	55.2
Sn K ₂ Cl ₆	..	409.2	"	0.133 Kp.	54.4
Cr ₂ Cl ₆	..	317.4	"	0.143 Kp.	45.4
Ag Br	..	188	Fused	0.0739 R.	13.9
K Br	..	119.1	"	0.1132 R.	13.5
Na Br	..	103	"*	0.1384 R.	14.3
Pb Br ₂	..	367	"	0.0533 R.	19.6
Ag I	..	235	"	0.0616 R.	14.5
Cu I	..	190.4	"	0.0687 R.	13.1
Hg I	..	327	Powder	0.0395 R.	12.9
K I	..	166.1	Fused	0.0819 R.	13.6
Na I	..	150	"	0.0868 R.	13.0
Hg I ₂	..	454	"	0.0420 R.	19.1
Pb I ₂	..	461	"	0.0427 R.	19.7
Ca Fl ₂	..	78	Fluor-spar	0.2082 N.	16.2
			"	0.2149 R.	16.8
Al Na ₃ Fl ₆	..	210.4	Cryolite	0.209 Kp.	16.3
Cu ₂ O	..	142.8	Red copper ore	0.238 Kp.	50.1
			"	0.1073 N.	15.3
H ₂ O	..	18	Ice between -21° and -2°	0.111 Kp.	15.9
			" 78° " 0°	0.480 Pr.	8.6
						0.474 R.	8.5

Desains found the specific heat of ice between -20° and 0° to be 0.513; Person, between -20° and 0° = 0.504; Hess, between -14° and 0° = 0.533. Person is of opinion that ice even somewhat below its melting-point, between -2° and 0°, absorbs heat of fusion.

Cu O	..	79.4	{	0.137 N.	10.9
			{	0.1420 R.	11.3
			{	0.128 Kp.	10.2
Hg O	..	216	{	Commercial	0.049 N.	10.6
			{	Crystalline	0.0518 R.	11.2
			{	"	0.0530 Kp.	11.4
Mg O	..	40	{	0.276 N.	11.0
			{	0.2439 R.	9.8
Mn O	..	71	{	0.1570 R.	11.1
Ni O	..	74.8	{	Feebly ignited	0.1623 R.	12.1
			{	Strongly ignited	0.1588 R.	11.9
			{	Fused	0.0509 R.	11.4
Pb O	..	223	{	Crystalline powder	0.0512 R.	11.4
			{	" "	0.0553 Kp.	12.3
Zn O	..	81.2	{	0.132 N.	10.7
			{	0.1248 R.	10.1
Mg O . H ₂ O	..	58	{	Brucite	0.312 Kp.	18.1
			{	Magnetic iron ore	0.1641 N.	38.1
Fe ₃ O ₄	..	232	{	" "	0.1678 R.	38.9
			{	" "	0.156 Kp.	36.2
Mg Al ₂ O ₄	..	142.8	{	Spinel	0.194 Kp.	27.7
Mg ₂ Fe ₂ Cr ₃ Al ₂ O ₄	..	196	{	Chrome iron ore	0.159 Kp.	31.2

* The preparation contained carbonate of sodium.

	Atomic weight.				Specific heat.	Atomic heat.
$\text{Al}_2 \text{O}_3$	102·8	{ Sapphire	0·1972 N.	20·3
$\text{As}_2 \text{O}_3$	198	{	0·2173 R.	22·3
$\text{B}_2 \text{O}_3$	69·8	{ Opaque	0·1279 R.	25·3
$\text{Bi}_2 \text{O}_3$	468	{ Fused	0·2374 R.	16·6
		{	0·0605 R.	28·3
$\text{Cr}_2 \text{O}_3$	152·4	{	0·196 N.	29·9
		{	0·1796 R.	27·4
		{ Crystalline	0·177 Kp.	27·0
		{ Artificial, feebly ignited	0·1757 R.	28·1
		{ .. strongly ignited	0·1681 R.	26·9
$\text{Fe}_2 \text{O}_3$	160	{ Specular iron	0·1692 N.	27·1
		{	0·1670 R.	26·7
		{	0·154 Kp.	25·1
$\text{Fe}_5 \text{Ti}_3 \text{O}_3$	155·5	{ Iserine	0·1762 N.	27·4
		{	0·177 Kp.	27·5
$\text{Sb}_2 \text{O}_3$	292	{ Fused	0·0901 R.	26·3
$\text{Mn}_2 \text{O}_3 \cdot \text{H}_2 \text{O}$	176	{ Manganite	0·176 Kp.	31·0
MnO_2	87	{ Pyrolusite	0·159 Kp.	13·8
		{ Quartz	0·1883 N.	11·3
SiO_2	60	{	0·1913 R.	11·5
		{	0·186 Kp.	11·2
$\text{Si}_2 \text{Zr}_2 \text{O}_2$	90·8	{ Zircon	0·1456 R.	13·2
		{	0·132 Kp.	12·0
		{ Cassiterite	0·0931 N.	14·0
SnO_2	150	{	0·0933 R.	14·0
		{	0·0894 Kp.	13·4
		{ Artificial	0·1716 R.	14·1
TiO_2	82	{ Rutile	0·1724 N.	14·1
		{	0·1703 R.	14·0
		{	0·157 Kp.	12·9
		{ Brookite	0·161 Kp.	13·2
MoO_3	144	{ Fused	0·1324 R.	19·1
		{ Pulverulent	0·154 ? Kp.	22·2
WO_3	232	{	0·0798 R.	18·5
		{	0·0894? Kp.	20·7

86. Carbonates and Silicates.

$\text{K}_2 \text{CO}_3$	138·2	{ Fused	0·2162 R.	29·9
		{	0·206 Kp.	28·5
$\text{Na}_2 \text{CO}_3$	106	{	0·2728 R.	28·9
$\text{Rb}_2 \text{CO}_3$	230·8	{	0·216 Kp.	26·1
BaCO_3	197	{ Witherite	0·1078 N.	21·2
		{	0·1101 R.	21·7
		{ Calc-spar	0·2046 N.	20·5
		{	0·2086 R.	20·9
CaCO_3	100	{	0·206 Kp.	20·6
		{ Arragonite	0·2018 N.	20·2
		{	0·2085 R.	20·9
		{	0·203 Kp.	20·3
$\text{Ca}_2 \text{Mg}_2 \text{CO}_3$	92	{ Bitter spar	0·2161 N.	19·9
		{	0·2179 R.	20·0
		{	0·206 Kp.	19·0
FeCO_3	116	{ Spathic iron	0·182 N.	21·1
		{	0·1934 R.	22·4

The minerals investigated doubtless contained part of the iron

replaced by metals of lower atomic weight. The atomic weight and the product assumed above are somewhat too great.

	Atomic weight.				Specific heat.	Atomic heat.
$\text{Fe}_{\frac{8}{11}}\text{Mn}_{\frac{2}{11}}\text{Mg}_{\frac{1}{11}}\text{CO}_3$	112·9	Spathic iron	0·166 Kp.	18·7
$\text{Mg}_{\frac{2}{7}}\text{Fe}_{\frac{2}{7}}\text{CO}_3$	91·1	Magnesite	0·227 N.	20·7
Pb CO_3	267	{ Cerussite	0·0814 N.	21·7
		"	0·0791 Kp.	21·1

Regnault found for precipitated carbonate of lead still containing water, the specific heat 0·0860.

Sr CO_3	147·6	{ Strontianite	0·1445 N.	21·3
		Artificial	0·1448 R.	21·4
Ca Si O_3	116	Wollastonite	0·178 Kp.	20·7
$\text{Ca}_{\frac{2}{3}}\text{Mg}_{\frac{1}{3}}\text{Si O}_3$	108	{ Diopside from Tyrol	0·1906 N.	20·6
		"	0·186 Kp.	20·1
$\text{Cu Si O}_3\cdot\text{H}_2\text{O}$	157·4	Diopside	0·182 Kp.	28·7
		Olivine	0·189 Kp.	27·6
$\text{Mg}_{\frac{2}{11}}\text{Fe}_{\frac{2}{11}}\text{Si O}_4$	145·8	{ Crysolite	0·189 Kp.	27·6
		"	0·2056 N.	30·0
		Adularia	0·1861 N.	103·7
$\text{Al}_2\text{K}_2\text{Si}_6\text{O}_{16}$	557	{ Orthoclase	0·1911 N.	106·4
		"	0·183 Kp.	101·9
$\text{Al}_2\text{Na}_2\text{Si}_6\text{O}_{16}$	524·8	{ Albite	0·1961 N.	102·9
		"	0·190 Kp.	99·7

87. Borates, Molybdates, Tungstates, Chromates, and Sulphates.

K BO_2	82	Fused	0·2048 R.	16·8
Na BO_2	65·9	"	0·2571 R.	16·9
$\text{Pb B}_2\text{O}_4$	292·8	"	0·0905 R.	26·5
$\text{Pb B}_4\text{O}_7$	362·6	"	0·1141 R.	41·4
$\text{K}_2\text{B}_4\text{O}_7$	233·8	"	0·2198 R.	51·4
$\text{Na}_2\text{B}_4\text{O}_7$	201·6	{ "	0·2382 R.	48·0
		"	0·229 Kp.	46·2
$\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$	381·6	Crystallised borax	0·385 Kp.	146·9
Pb Mo O_4	367	Yellow lead ore	0·0827 Kp.	30·4
Ca WO_4	288	Scheelite	0·0967 Kp.	27·9
$\text{Fe}_{\frac{2}{3}}\text{Mn}_{\frac{1}{3}}\text{WO}_4$	333·4	{ Tungsten	0·0930 Kp.	28·2
		"	0·0978 R.	29·7

The locality of the wolfram investigated by Regnault is not known, and the composition uncertain. But the change in the ratio in which iron and manganese are present in the mineral alters little in the atomic weight.

Pb Cr O_4	323·4	Fused	0·0900 Kp.	29·0
$\text{K}_2\text{Cr O}_4$	194·4	{ Crystallised	0·1851 R.	36·0
		"	0·189 Kp.	36·7
$\text{K}_2\text{Cr}_2\text{O}_7$	294·6	{ "	0·1894 R.	55·8
		"	0·186 Kp.	54·8
K H S O_4	136·1	"	0·244 Kp.	33·2

	Atomic weight.		Specific heat.	Atomic heat.
$K_2 S O_4$..	174·2	{ Fused	0·1901 R.	33·1
		{ Crystallised	0·196 Kp.	34·1
$Na_2 S O_4$..	142	{ Fused	0·2312 R.	32·8
		{ Crystallised	0·227 Kp.	32·2
$Nu_2 H_8 S O_4$..	132	"	0·350 Kp.	46·2
$Ba S O_4$..	233	{ Heavy spar	0·1088 N.	25·4
		"	0·1128 R.	26·3
		"	0·108 Kp.	25·2
$Ca S O_4$..	136	{ Calcined gypsum	0·1966 R.	26·7
		{ Anhydrite	0·1854 N.	25·2
		"	0·178 Kp.	24·2
$Cu S O_4$..	159·4	{ Solid pieces	0·184 Pp.	29·3
$Mg S O_4$..	120	{ Dehydrated salt	0·2216 R.	26·6
		{ Solid pieces	0·225 Pp.	27·0
$Mn S O_4$..	151	"	0·182 Pp.	27·5
$Pb S O_4$..	303	{ Artificial	0·0872 R.	26·4
		{ Lead-vitriol	0·0848 N.	25·7
		"	0·0827 Kp.	25·1
$Sr S O_4$..	183·6	{ Artificial	0·1428 R.	26·2
		{ Celestine	0·1356 N.	24·9
		"	0·135 Kp.	24·8
$Zn S O_4$..	161·2	{ Coarse powder	0·174 Pp.	28·0
$Cu S O_4 \cdot H_2 O$..	177·4	Pulverulent	0·202 Pp.	35·8
$Mg S O_4 \cdot H_2 O$..	138	Coarse powder	0·264 Pp.	36·4
$Zn S O_4 \cdot H_2 O$..	179·2	Solid pieces	0·202 Pp.	36·2
$Ca S O_4 \cdot 2 H_2 O$..	172	{ Gypsum	0·2728 N.	46·9
		"	0·259 Kp.	44·6
$Cu S O_4 \cdot 2 H_2 O$..	195·4	Pulverulent	0·212 Pp.	41·4
$Zn S O_4 \cdot 2 H_2 O$..	197·2	Solid pieces	0·224 Pp.	44·2
$Fe S O_4 \cdot 3 H_2 O$..	206	"	0·247 Pp.	50·9
$Cu S O_4 \cdot 5 H_2 O$..	249·4	{ Crystallised	0·285 Kp.	71·1
		"	0·316 Pp.	78·8
$Mn S O_4 \cdot 5 H_2 O$..	241	"	0·323 Kp.	77·8
		"	0·338 Pp.	81·5
$Ni S O_4 \cdot 6 H_2 O$..	262·8	"	0·313 Kp.	82·3
$Co S O_4 \cdot 7 H_2 O$..	280·8	"	0·343 Kp.	96·4
$Fe S O_4 \cdot 7 H_2 O$..	278	{ "	0·346 Kp.	96·2
		"	0·356 Pp.	99·0
$Mg S O_4 \cdot 7 H_2 O$..	246	{ "	0·362 Kp.	89·1
		"	0·407 Pp.	100·1
$Zn S O_4 \cdot 7 H_2 O$..	287·2	{ "	0·347 Kp.	99·7
		"	0·328 Pp.	94·2
$MgK_2S_2O_8 \cdot 6H_2O$..	402·2	"	0·264 Kp.	106·2
$NiK_2S_2O_8 \cdot 6H_2O$..	437	"	0·245 Kp.	107·1
$ZnK_2S_2O_8 \cdot 6H_2O$..	443·4	"	0·270 Kp.	119·7
$Al_2K_2S_4O_{16} \cdot 24H_2O$..	949	" alum	0·371 Kp.	352·1
$Cr_2K_2S_4O_{16} \cdot 24H_2O$..	998·6	" chrome alum ..	0·324 Kp.	323·6

88. *Arseniates, Phosphates, Pyrophosphates and Metaphosphates, Nitrates, Chlorates, Perchlorates, and Permanganates.*

$K As O_3$..	162·1	Fused	0·1563 R.	25·3
$K H_2 As O_4$..	180·1	Crystallised	0·175 Kp.	31·5
$Pb_3 As_2 O_8$..	899	Fused	0·0728 R.	65·4
$Ag_3 P O_4$..	419	Pulverulent	0·0896? Kp.	37·5
$K H_2 P O_4$..	136·1	Crystallised	0·280 Kp.	28·3
$Na_2 H P O_4 \cdot 12 H_2 O$..	358	Between -21° and 22° ..	0·408 Pr.	146·1

The determination of the specific heat refers to the crystallised salt. For the fused and afterwards solidified salt Person found the specific heat between the same range of temperature considerably greater, = 0·68 to 0·78; but the mass obtained by solidifying the fused salt gradually alters (it becomes crystallised again) with increase of volume, which is very considerable when the fused salt is allowed to cool very rapidly.

	Atomic weight.					Specific heat.	Atomic heat.
$\text{Pb}_3 \text{P}_2 \text{O}_8$	811	0·0798 R.	64·7
$\text{K}_4 \text{P}_2 \text{O}_7$	330·4	..	Fused	0·1910 R.	63·1
$\text{Na}_4 \text{P}_2 \text{O}_7$	266	0·2283 R.	60·7
$\text{Pb}_2 \text{P}_2 \text{O}_7$	588	0·0821 R.	48·3
Na P O_3	102	0·217 Kp.	22·1
$\text{Ca P}_2 \text{O}_6$	198	0·1992 R.	39·4
Ag N O_3	170	0·1435 R.	24·4
K N O_3	101·1	{	0·2388 R.	24·1
			0·227 Kp.	22·9
			Crystallised	0·232 Kp.	23·5
$\text{K}_{\frac{1}{2}} \text{Na}_{\frac{1}{2}} \text{N O}_3$	93	{	Fused*	0·235 Pr.	21·9
			0·2782 R.	23·6
			0·256 Kp.	21·8
Na N O_3	85	{	0·257 Kp.	21·8
			Crystallised	0·455 Kp.	36·4
			0·1523 R.	39·8
$\text{N}_2 \text{H}_4 \text{O}_3$	80	{	0·145 Kp.	37·9
$\text{Ba N}_2 \text{O}_6$	261		0·110 Kp.	36·4
$\text{Pb N}_2 \text{O}_6$	331		0·181 Kp.	38·3
$\text{Sr N}_2 \text{O}_6$	211·6	{	0·2096 R.	25·7
			Fused	0·194 Kp.	23·8
			Crystallised	0·157 Kp.	50·6
$\text{Ba Cl}_2 \text{O}_6 \cdot \text{H}_2 \text{O}$	322	{	0·190 Kp.	26·3
K Cl O_4	138·6		0·179 Kp.	28·3
K Mn O_4	158·1			

89. So-called Organic Compounds.

$\text{Hg C}_2 \text{N}_2$	252	..	Crystallised cyanide of mercury	0·100	Kp.	25·2
$\text{Zn K}_2 \text{C}_4 \text{N}_4$	247·4	{	.. cyanide of zinc and	0·241	Kp.	59·6
			potassium			
$\text{Fe K}_3 \text{C}_6 \text{N}_6$	329·3		Crystallised ferricyanide of po-			
		{	tassium	0·233	Kp.	76·7
$\text{FeK}_4 \text{C}_6 \text{N}_6 \cdot 3 \text{H}_2 \text{O}$	422·4		Crystallised ferrocyanide of po-			
			tassium			
$\text{C}_2 \text{Cl}_6$	237	..	Between 18° and 37° ..	0·178	Kp.	42·2

The specific heat between 18° and 43° was found = 0·194; between 18° and 50° = 0·277.

$\text{C}_{10} \text{H}_8$	128	..	Between - 26° and 18°	0·3096	A.	39·6
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* Obtained as mass of constant melting-point (219°·8) by fusing equivalent quantities of nitrate of potass and nitrate of soda.

The specific heat of naphthalene was found to be 0·3208 between 0° and 20, and 0·3208 between 20° and 65°.

	Atomic weight.		Specific heat.	Atomic heat.
$C_{27}H_{54}O_2$.. 410	{ Between - 21° and 3°	.. 0·4287 Pr.	{ 175·8
$C_{46}H_{92}O_2$.. 676			
				{ 289·8

The first formula is that of one constituent of bees'-wax, cerotic acid; the second is that of the other, palmitate of melissyl. With reference to the numbers found for the specific heat of bees'-wax at higher temperatures, compare the last remark in § 77.

$C_{12}H_{22}O_{11}$.. 342	{ Crystallised cane-sugar	.. 0·301	Kp.	102·9
			.. 0·342	Kp.	117·0
$C_6H_{14}O_6$.. 182	Mannite 0·324	Kp.	59·1
$C_4H_6O_4$ 118	Succinic acid 0·313	Kp.	36·9
$C_4H_6O_6$ 150	Tartaric acid 0·288	Kp.	43·2
$C_4H_6O_6 \cdot H_2O$.. 168	Racemic acid 0·319	Kp.	53·6
$C_2H_2BaO_4$.. 227	Formate of barium 0·143	Kp.	32·5
$C_2K_2O_4 \cdot H_2O$.. 184·2	Neutral oxalate of potassium 0·236	Kp.	43·5
$C_4H_3KO_8 \cdot 2H_2O$	254·1	Quadroxalate of potassium 0·283	Kp.	71·9
$C_4H_5KO_6$.. 188·1	Acid tartrate of potassium 0·257	Kp.	48·3
$C_4H_4NaKO_6 \cdot 4H_2O$	282·1	Seignette salt 0·328	Kp.	92·5
$C_8H_{10}CaO_{10} \cdot 8H_2O$	450	Acid malate of calcium 0·338	Kp.	152·1

The preceding tables contain the material, obtained experimentally, which serves as subject and basis for the subsequent considerations on the relations of the specific heat of solid bodies to their atomic weight and composition.

PART V.—On the Relations between Atomic Heat and Atomic Weight or Composition.

90. I discuss in the sequel the regularities exhibited by the atomic heats of solid bodies, the exceptions to these regularities, and the most probable explanation of these exceptions. With regard to the views which are here developed, much has been already expressed or indicated in former speculations; in this respect I refer to the first part of this paper, in which I have given the views of earlier inquirers as completely as I know them, and as fully as was necessary to bring out the peculiar value of each. It is unnecessary, then, to refer again to what was there given; but I will complete for individual special points what is to be remarked from an historical point of view.

But before discussing these regularities, the question must be discussed whether the atomic heat of a given solid substance is

essentially constant, or varies materially with its physical condition. It depends on the result of this investigation, how far it may with certainty be settled whether the general results already obtained are of universal validity, or whether exceptions to them exist.

The specific heat of a solid body varies somewhat with its temperature : but the variation of the specific heat with the temperature is very small, provided the latter does not rise so high that the body begins to soften. Taking the numbers obtained by Regnault for lead, by Dulong and Petit, by Bede and by Byström, for the specific heats of several metals at different temperatures, the conviction follows that the changes of specific heat, if not of themselves inconsiderable, are yet scarcely to be regarded in comparison with the discrepancies in the numbers which different observers have found for the specific heat of the same body at the same temperature. At temperatures at which a body softens, the specific heat does indeed vary considerably with the temperature (compare for example § 77) ; but these numbers, as containing already part of the latent heat of fusion, give no accurate expression for the specific heat, and are altogether useless for recognising the relations between this property and the atomic weight or composition.

Just as little need the small differences be considered which Regnault found for a few metallic substances according as they were hammered or annealed, hard or soft.

For dimorphous varieties of the same substance, even where there are considerable differences in the specific gravity, the specific heats have not been found to be materially different (see FeS_2 , § 83 ; TiO_2 , § 85 ; CaCO_3 , § 86). The results obtained with these substances appear to me more trustworthy than those with graphite and the various modifications of boron and silicium, which moreover have given partly the same specific heat for the graphitoid and adamantine modification of the same element. What trustworthy observations we now possess decidedly favour the view that the dimorphic varieties of the same substance have essentially the same specific heat.

91. It has been surmised that the same substance might have an essentially different specific heat in the amorphous and crystalline states. I believe that the differences of specific heat found for these different conditions depend, to by far the greatest extent, upon other circumstances.

The tables in § 83 to § 89 contain a tolerable number of substances which have been investigated both after being melted and also crystallised; there are no such differences in the numbers as to lead to the supposition that the amorphous solidified substance had a different specific heat to what it had in the crystallised state. No such influence of the state has been with any certainty shown to affect the validity of Dulong and Petit's, or of Neumann's law. I may here again neglect what the determinations of carbon, boron, or silicium appear to say for or against the assumption of a considerable influence of the amorphous or crystalline condition on the specific heat. Regnault found (§ 85) that the specific heat of artificially prepared (uncrystalline?) and crystallised titanitic acid did not differ. According to my investigations (§ 48), silicic acid has almost the same specific heat in the crystallised and in the amorphous condition.

In individual cases, where the specific heat of the same substance for the amorphous and crystallised modification has been found to be materially different*, it may be shown that foreign influences affected the determination for the one condition. Such influences are especially: 1. That one modification absorbed heat of softening at the temperature of the experiment; that is doubtless the reason why the specific heat of yellow phosphorus was found to be considerably greater at higher temperatures than that of red phosphorus, but not at low temperatures (compare § 82), that the specific heat of amorphous cane-sugar was found to be decidedly greater than that of the crystallised variety (§ 78), and, according to Regnault's opinion, also that the specific heat of amorphous selenium between 80° and 18° was found much greater ($= 0.103$) than that of the crystalline, while for lower temperatures there was no difference in the specific heats of the two substances (§ 82). 2. That in heating one modification, its transition into the other is induced, and the heat liberated in this transition makes the numbers for the specific heat incorrect; in § 33 I have discussed the probability that this circumstance, in Regnault's first experiments with sulphur, gave the specific heat much too

* De la Rive and Marcet (Ann. Ch. Phys. [2] lxxv, 118) found the specific heat of vitreous to be different from that of opaque arsenious acid, and considered the fact to be essential; but their method was not fitted to establish such a difference. Pape's view, too (Pogg. Ann. exx, 341 and 342), that it is of essential importance for the specific heat of hydrated sulphates whether the salts are crystallized or not, does not appear to me to be proved by what he has adduced.

high, and it is possible that it was also perceptible in the above-mentioned experiments with amorphous selenium. 3. That in immersing heated porous bodies in the water of the calorimeter heat becomes free (compare § 19); I consider this as the reason why Regnault found the specific heat of the more porous forms of carbon so much greater than that of the more compact forms (compare § 36); and Regnault himself sees in this the reason why he found the specific heat of the feebly ignited and porous oxides of nickel and of iron greater than that of the same oxides after stronger heating (compare § 85).

From the importance of this subject for the considerations to be afterwards adduced, I have here had to discuss more fully what differences are real and what are only apparent in the numbers found for the specific heat of one and the same substance. Even if the apparent differences are often considerable, their importance diminishes, if allowance is made for the foreign influence which may have prevailed. In many cases, on the other hand, a body in totally different modifications has almost exactly the same specific heat if these foreign influences are excluded. It may, then, be said that, from our present knowledge, one and the same body may exhibit small differences with certain physical circumstances (temperature, different degree of density), but never so great that they may be taken as an explanation why a body decidedly and undoubtedly forms an exception to a regularity which might have perhaps been expected for it—provided that the determination of the specific heat, according to which the body in question forms an exception, is trustworthy, and kept free from foreign influences.

92. Among the regularities in the atomic heat of solid bodies, that found by Dulong and Petit for the elements stands foremost. A glance at the atomic heats of the so-called elements collated in § 82, shows that, for by far the greater number, the atomic heats are in fact approximately equal. But the differences in the atomic heats, even of those elements which are usually regarded as coming under Dulong and Petit's law, are often very considerable, even when the comparison is limited to those which are most easily obtained in a pure state, and even if numbers are taken for the specific heats which give the most closely agreeing atomic heats. Regnault* sought an explana-

* Ann. Ch. Phys. [2] lxxiii, 66, and [3] xlv. 257.

tion of the differences of the atomic heats of the elements in the circumstance that the latter could not be investigated in comparable conditions of temperature and density ; further, that the numbers for the specific heat, as determined for solid bodies, contain, besides the true specific heat (for constant volume), also the heat of expansion. As specific heat we can indeed only take the sum of the heats necessary for heating and for expansion. But it is not yet proved that the products of the first quantity (the specific heat for constant volume) and the atomic weights would agree better than the atomic heats now do ; it is only a supposition, and even the very contrary may be possible with individual substances. Temperature has an influence on the specific heat of solid bodies, and to a different extent with different bodies. Even in this respect, also, all means are wanting by which the different temperatures at which bodies are really comparable can be known, and a comparison made of their atomic heats. The utmost possible is to determine the specific heat at such a distance from the melting point that latent heat of softening can have no influence. It is impossible to say with certainty whether the atomic heats of bodies compared at other temperatures than those which are nearly identical (ranging about 90° on each side of 10°) will show a closer agreement. It is not probable. Changes in the specific heat of solid bodies, so long as they are unaffected by heat of softening, are small in comparison with the differences which the atomic heats of individual elements show. And it is well worth consideration that individual elements (phosphorus and sulphur, *e.g.*) at temperatures relatively near their melting points, have not materially greater specific heats than other elements (iron and platinum, for example) at temperatures relatively distant from their melting points, but, on the contrary, considerably smaller. As regards the influence of density on the specific heat, it is undoubtedly certain that the latter may somewhat vary with the former ; but it is equally so that in all cases in which substances of undoubted purity were examined and the sources of error mentioned (§ 91) excluded, this variation is too inconsiderable to give an adequate explanation of the differences of the atomic heats found for the various solid elements.

I need not here revert to the considerations developed in §§ 90 and 91, as to how far a difference in the physical condition of a solid substance exercises an essential influence on its specific heat ; for whatever view may be held with reference to this influence,

and generally with reference to the circumstances which alter the specific heat of a substance, and therewith the atomic heat, this is certain, that there are individual elements whose atomic heat is distinctly and decidedly different from that of most other elements. Such elements are, from § 82, first of all boron, carbon, and silicium.

The decision of the question whether these elements really form exceptions to Dulong and Petit's law presupposes, besides a knowledge of their specific heat, a knowledge of their atomic weight also. There can be no exceptions to Dulong and Petit's law, if, regardless of anything which may be in opposition to it, the principle is held to, that the atomic weights of the elements must be so taken as to agree with this law. As a trial whether this law is universally applicable, the atomic weights ought rather to be taken as established in another manner. It may be confessed that the determination of the true atomic weights by chemical and physico-chemical investigations and considerations is still uncertain, and many questions are still unanswered the settlement of which may influence that determination. But there seems now to be no more trustworthy basis for fixing the atomic weights of the elements than that of taking, as the atomic weights of the elements, the relatively smallest quantities which are contained in equal volumes of their gaseous or vaporous compounds, or of which the quantities contained in such volumes are multiples of the smallest numbers; and no better means appears to exist for determining the atomic weights of those elements the vapour-densities of whose compounds could not be determined, than the assumption that in isomorphous compounds the quantities of the corresponding elements are as the atomic weights of the latter. On this basis, and using this means, the numbers for the atomic weights have been determined which are contained in the last column of the Table in § 2, and are used in § 82 *et seq.* The atomic weights $B = 10.9$, $C = 12$, $Si = 28$, cannot be changed for others. That the atomic weights of tin and silicium are as 118 to 28, is further proved by the isomorphism of the double fluorides. But to these atomic weights correspond atomic heats which are far smaller than those found for most other elements. From the chemical point of view it is inadmissible to take the atomic weights of boron, carbon, and silicium* in such a manner as to make their

* For Regnault's observation, whether, considering the specific heat which he found for silicium, its atomic weight is to be so taken that silicic acid contains

atomic heats agree with Dulong and Petit's law. In any case these three elements form exceptions to Dulong and Petit's law. The sequel will show that this is the case with many other elements.

93. In many compounds the regularity is observed, that by dividing their atomic heat by the number of elementary atoms contained in one molecule of the compound, a quotient is obtained which comes very near the atomic heat of most of the elements—that is, 6·4. This is found in the alloys enumerated in § 82, and also in a great number of compounds of definite proportions. A few of the most important cases may be given here. For

smaltine, CoAs_2 (compare § 83), this quotient is $\frac{19\cdot2}{3} = 6\cdot4$;

for the chlorine-compounds, RCl and RCl^* , the mean of the atomic heats given in § 84 is 12·8, and the quotient $\frac{12\cdot8}{2} = 6\cdot4$.

Of the chlorine-compounds, RCl_2 , the mean atomic heat of all the determinations in § 84 is 18·5, and the quotient $\frac{18\cdot5}{3} = 6\cdot2$.

It is also very near this value in the double chlorides; in ZnK_2Cl_4 it is $\frac{43\cdot4}{7} = 6\cdot2$, for RK_2Cl_6 (the mean of the determinations of

PbK_2Cl_6 and SnK_2Cl_6) it is $\frac{54\cdot8}{9} = 6\cdot1$. For bromine-compounds,

RBr (both here and in the following examples the means are taken of the determinations in § 84), $\frac{13\cdot9}{2} = 6\cdot9$; for PbBr_2 ,

$\frac{19\cdot6}{3} = 6\cdot5$; for iodine-compounds, RI and RI , $\frac{13\cdot4}{2} = 6\cdot7$,

and for the iodine-compounds, RI_2 , $\frac{19\cdot4}{3} = 6\cdot5$.

But this regularity, though met with in many compounds, is by no means universal. The oxygen-compounds of the metals correspond to it in general the less, the greater the number of oxygen-atoms they contain as compared with that of metal. The

2 atoms of silicium to 5 of oxygen, compare Ann. Chim. Phys. [3] v. lxiii, 30. For Scheerer's remark, that according to the most probable specific heat of silicium its atomic weight must be taken so that for 1 atom of silicium there are 3 atoms of oxygen, compare Poggendorff's Annalen, vol. cxviii, p. 182.

* In the sequel R stands for a uni-equivalent, and R for a polyequivalent atom of a metal.

mean atomic heat of the oxides RO in § 85 is 11.1, and the quotient $\frac{11.1}{2} = 5.6$. The quotient for the oxides R_2O_3 and R_2O_3 (even excluding the determinations of alumina and boracic acid) is only $\frac{27.2}{5} = 5.4$; for the oxides RO_2 (even excluding the determinations for silicic acid and zircon) only $\frac{13.7}{3} = 4.6$; for the oxides RO_3 , the mean of Regnault's determinations only $\frac{18.8}{4} = 4.7$. Still smaller is the quotient for compounds which contain boron in addition to oxygen (*e.g.* for the compounds R BO_2 (compare § 87) it is only $\frac{16.8}{4} = 4.2$; for boracic acid, B_2O_3 , it is only $\frac{16.6}{5} = 3.3$); also for compounds which contain silicon in addition to oxygen (it is $\frac{11.3}{3} = 3.8$ for silicic acid, Si O_2 , compare § 85), or which contain oxygen as well as hydrogen (for ice, H_2O , it is only $\frac{8.6}{3} = 2.9^*$, compare § 85), or which contain hydrogen and carbon besides oxygen (*e.g.*, it is only $\frac{36.9}{14} = 2.6$ for succinic acid, $\text{C}_4\text{H}_6\text{O}_4$, compare § 82). We may state in a few words which are the cases in which this quotient approximates to the atomic heat of most elements, and which the cases in which it is smaller. It is near 6.4 in those compounds which only contain elements whose atomic heats, corresponding to

* Considering the atomic heat of liquid water to be 18, Garnier (Compt. rend. xxxv. 278) thought that the quotient obtained by dividing the atomic weight by the number of elementary atoms in one atom of the compound, $\frac{18}{3} = 6$, came near the atomic heat of the elements. But it requires no explanation to show that, in a comparison with the atomic heats of solid elements and solid compounds, that atomic heat must be taken for the compound H_2O which is obtained from the specific heat of ice, and not from that of water. Garnier is not alone in his error, which is rather to be ascribed to the circumstance that, formerly in considering the influence of composition or the specific heat of compounds, solid and liquid bodies were regarded as comparable in respect of their specific heat. Hermann more especially (Nouveaux Mémoires de la Société des Naturalistes de Moscou, vol. iii, p. 137) compared liquid water with solid compounds, as did also Schröder (Pogg. Ann. lii, 279); so likewise did L. Gmelin, in an early discussion of this subject (Gehler's Physikalische Wörterbuch, neue Bearbeitung, vol. iv, p. 1942) while he subsequently (Handbuch der Chemie, 1. Aufl., vol. i, p. 220) more correctly compared the specific and the atomic heat of ice with that of other solid compounds.

Dulong and Petit's law, are nearly equal to 6.4; it is smaller in compounds which contain elements not coming under Dulong and Petit's law, and having a much smaller atomic heat than 6.4, and which are recognised as exceptions to this law, either directly, if their specific heat has been determined for the solid state (compare § 92), or indirectly, if it be determined in the manner to be subsequently described.

94. The determinations of specific heat given in §§ 83 to 89 contain the proofs hitherto recognised for the law that chemically-similar bodies of analogous atomic constitution have approximately the same atomic heat; and a considerable number of new examples of the prevalence of this regularity are given by my determinations. The groups of analogous compounds need not again be collated, as Neumann has done for a smaller and Regnault for a larger number of groups and for individual elements contained in them. What I will here discuss is the prevalence, beyond the limits of our previous knowledge, of the regularity, that compounds of analogous atomic constitution have approximately the same atomic heat.

To this belongs, first, the existence of this regularity in the case of chemically similar bodies, which exhibit an analogy of atomic constitution, when their formulæ are written with the atomic weights admitted in recent times for the elements, but which could not be recognized so long as the equivalents of the elements were taken as a basis, or the formula written, as by Regnault, with the use of the so-called thermal atomic weights.

The approximate equality of the atomic heats of analogous nitrates and chlorates, of the alkalies, for example, had been already observed. The same character, the haloid, is ascribed both to carbonates and to silicates; but as their formulæ were formerly written, an analogy in the composition of chlorates and nitrates, or carbonates and silicates, could not be assumed. But salts of these four different classes, as well as arseniates and metaphosphates, have analogous atomic constitutions if we assume the recent atomic weights. The same salts have then also approximately equal atomic heats. We get the atomic heat

Of chlorate of potassium, KClO_3 , § 88	M^* 24.8
„ the nitrates, RNO_3 , in § 88	M 23.0

* M signifies the mean of all determinations.

Of metaphosphate of sodium, NaPO_3 , § 88	22·1
„ arseniate of potassium, KAsO_3 , § 88	25·3
„ the carbonates, R_2CO_3 , § 86	M 20·7
„ the silicates, R_2SiO_3 , § 86	M 20·5

The differences in these approximately concordant atomic heats are partly essential and explainable. I shall return to this point (§ 95).

According to the more recent assumptions for the atomic weights, certain perchlorates, permanganates, and sulphates have an analogous atomic composition, and these salts have also approximately equal atomic heats; this has been found to be—

For perchlorate of potassium, KClO_4 , § 88	26·3
„ permanganate of potassium, KMnO_4 , § 88	..	28·3
„ the sulphates, R_2SO_4 , named in § 88	M 26·1

But approximate equality in the atomic heat is found, not only in such compounds of analogous chemical composition as have similar chemical character, but also in such as have totally dissimilar chemical character.

The chemical character of ferroso-ferrie oxide (magnetic iron ore) is quite different from that of neutral chromate of potassium. Ferrie oxide and arsenious anhydride have a chemical character totally different from nitrates or arseniates, or bodies of similar constitution. But for the first-named and for the last-named compounds, as respectively compared with each other, there is analogy in chemical composition and approximate equality of atomic heat. The atomic heat has been found to be—

For magnetic iron ore, Fe_3O_4 , § 85	M 37·7
„ chromate of potassium, K_2CrO_4 , § 87	M	36·4
„ sesquioxide of iron, Fe_2O_3 , § 85	M 26·8
„ arsenious oxide, As_2O_3 , § 85 25·3
„ the nitrates, RNO_3 , named in § 88 23·0
„ arseniate of potassium, KAsO_3 , § 88	25·3

But there is even in a more extended sense approximate equality of atomic heat in bodies of analogous atomic composition. If the formulae of the oxides, R_2O_2 (oxide of tin for instance) are doubled, they become R_2O_4 , and are then analogous to those of the sulphates, R_2SO_4 , or of tungstate of lime or of perchlorate of

potassium and other salts. To the formulæ thus made analogous equal atomic heats correspond. The following atomic heats have been found :—

Oxide of tin, Sn_2O_4 , compare § 85	M	27·6
Titanic oxide, Ti_2O_4 , „	M	27·3
The sulphates, R_2SO_4 , in § 87	M	26·1
Tungstate of calcium, CaWO_4 , compare § 87	27·9
Perchlorate of potassium, KClO_4 , compare § 88	26·3
Permanganate of potassium, KMnO_4 , compare § 88	28·3

If the formulæ of the oxides, RO_2 , are trebled, they become R_3O_6 , analogous to those of the nitrates RN_2O_6 (nitrate of barium, *e.g.*), and similar salts. Here also approximately equal atomic heats correspond to the formulæ thus made analogous. The atomic heats are as follows :—

Oxide of tin, Sn_3O_6 , compare § 85	M	41·4
Titanic oxide, Ti_3O_6 , „	M	41·0
The nitrates, $\text{R}_2\text{N}_2\text{O}_6$, in § 88	M	38·1
Metaphosphate of calcium, CaP_2O_6 , compare § 88	39·4

How little the atomic heat of compounds depends on their chemical character may be proved from a more extended series of examples than those adduced in the preceding. It is, however, unnecessary to dwell upon this. The comparisons and considerations contained in the sequel complete what has here been developed as a proof of the principle that the atomic heat of bodies is independent of their chemical character.

95. The foregoing comparisons give examples of cases in which bodies of analogous atomic structure, with a totally different chemical character, have approximately the same atomic heat; they show that with reference to the atomic heat, uni-equivalent and multi-equivalent elementary atoms have the same influence, which, indeed, followed already from Regnault's comparisons; that the atomic heat of a substance for its multifold atomic formula may be compared with that of another substance for a simple atomic formula. The preceding contains a generalization of Neumann's law; but as certainly as this law is recognised in the preceding in a more general manner than was formerly assumed, as little is it universally applicable.

Regnault's investigations have shown that Neumann's law is

not rigidly valid. Even for those compounds which contain the same element as electronegative constituent, and have similar atomic constitution, he found the atomic heats as much as $\frac{1}{10}$ to $\frac{1}{9}$ different from each other.* The reason of this he seeks in the same circumstances, which in his view prevent a closer agreement in the atomic weights of the elements (compare § 92).

Differences of this kind, and even of greater amount, occur in the atomic heats of compounds for which closer agreement in these numbers might be expected—of such compounds, that is, as contain elements of the same, or nearly the same atomic heat combined with the same other element in the same atomic proportion. To this belongs the fact that the atomic heat has been found so different (§ 85) for the isomorphous compounds, magnetic iron ore (37·7), chrome iron ore (31·2), and spinelle (27·7), and for alumina (21·3) and for sesquioxide of iron (26·8). In the atomic heats of such analogous compounds there are differences for which, or rather for the magnitude of which, as furnished by our present observations, I know at present no adequate explanation.

But there is another kind of difference in the atomic heats of analogous compounds, which exhibits a regularity, and for which an explanation can be given. Certain elements impress on all their compounds the common characteristic, that their atomic heat is much smaller than that of most analogous compounds. The atomic heat of boracic anhydride, B_2O_3 , is only 16·6, while that of most other compounds, R_2O_3 and R_2O_3 , is between 25 and 28 (§ 85). The atomic heat of the borates $R B O_2$, is (§ 87) only 16·8, while that of R_2O_2 , as the mean of the determination in § 85, is 22·2. The atomic heat of PbB_2O_4 is (§ 87) only 26·5, while that of Fe_3O_4 (§ 85) in the mean is 37·7. Similar results have been obtained for compounds of certain other elements, of carbon and of silicum, for instance, that is, of those elements which in the free state have a smaller atomic heat than that of most other elements.

This observation leads to the question whether the elements enter into compounds with the atomic heats which they have in the free state, and in connexion with this, how far is it permissible to make an indirect determination of the atomic heat of the elements (in their solid state) from the atomic heats of their (solid) compounds.

* Ann. Ch. Phys. [3], i, 196.

96. The assumption that elements enter into compounds with the atomic heats they have in the free state would be inadmissible, if not only the atomic structure as expressed by the empirical formula, but also the grouping of the elements to proximate constituents, as is endeavoured to be expressed by the rational formula, influenced the atomic heat of the compounds. That the latter is not the case is very probable from the comparisons made in § 94, where approximately equal atomic heats were obtained for compounds of analogous empirical formulæ, even with the greatest dissimilarity of chemical character. That that, which may be supposed and expressed by the so-called rational formula in reference to the internal constitution of compounds, does not affect the atomic heat, becomes more probable from the fact that chemically similar, and even isomorphous compounds, one of which contains an atomic group in the place of an individual atom in the other, exhibit dissimilar atomic heats. This is seen, for instance, in comparing analogous chlorine and cyanogen compounds ($\text{Cy}=\text{CN}$) the latter have far greater atomic heats. Thus the atomic heat

Of chloride of mercury, HgCl_2 , § 84, is	18.0
„ cyanide of mercury, HgCy_2 , § 89	25.2
„ chloride of zinc and potassium, ZnK_2Cl_4 , § 84	43.4
„ cyanide of zinc and potassium, ZnK_2Cy_4 , § 89	59.6

In like manner ammonium-compounds ($\text{Am}=\text{NH}_4$) have atomic heats considerably greater than the corresponding potassium-compounds. This is seen from the following Table:—

Chloride of potassium, KCl , § 84	M	12.9
„ ammonium, AmCl , § 84		20.0
Nitrate of potassium, KNO_3 , § 88	M	23.5
„ ammonium, AmNO_3 , § 88		36.4
Sulphate of potassium K_2SO_4 , § 87	M	33.6
„ ammonium, Am_2SO_4 , § 87		46.2

97. That undecomposable atoms and atomic groups are contained in compounds with the atomic heats they have in the free state, is further probable from the fact that the sum of the atomic heats of such atoms, or atomic groups, as when united form a certain compound, is equal or approximately equal to the atomic heat of this compound. For many compounds whose elements obey Dulong and

Petit's law, what has been stated in § 93 contains the proof that the atomic heat of these compounds is equal to the sum of the atomic heats of the elementary atoms contained in one atom of the compounds. That this is also observed when atomic groups are supposed to be united, forming more complicated compounds, will be seen by bringing forward a few examples. The atomic heat has been found—

For the oxides, RO , enumerated in § 85	M	11·1
„ sesquioxide of iron, Fe_2O_3 , § 85	M	26·8
Sum for FeRO_4			37·9
„ magnetic iron ore, Fe_3O_4 , § 85	M	37·7
„ the oxides, RO , in § 85	M	11·1
„ the acids, RO_3 , in § 85, according to Regnault		M	18·8
Sum for RRO_4			29·9
„ chromate of lead, PbCrO_4 , § 87		29·0
„ the oxides named in § 85, RO	M	11·1
„ binoxide of tin, SnO_2 , § 85	M	13·8
Sum for RRO_3			24·9
„ sesquioxide of iron, Fe_2O_3 , § 85	M	26·8
„ chromate of potassium, K_2CrO_4 , § 87	M	36·4
„ the anhydrides RO_3 , in § 85 (Regnault)		18·8
Sum for K_2CrRO_7			55·2
„ acid chromate of potassium, $\text{K}_2\text{Cr}_2\text{O}_7$, § 87..		M	53·3
„ binoxide of tin, Sn_3O_6 , § 85	M	41·4
„ base, R_2O_2 , mean of determinations, § 85 ..		M	22·2
Sum for R_5O_8			63·6
„ arseniate of lead, $\text{Pb}_3\text{As}_2\text{O}_8$, § 88.....		65·4

To this belongs the fact that water is contained in solid compounds with the atomic heat of ice.* The different determinations of the specific heat of this substance (§ 85) gave the atomic

* Even before Person (compare § 14) L. Gmelin had speculated (*Handbuch der Chemie*, [4] Aufl. vol. i, p. 223) whether from the atomic heats of anhydrous sulphate of calcium and of ice that of gypsum could be calculated. The results of calculation deviated considerably from the atomic heat as deduced from the observed specific heat of gypsum; the specific heat, and therewith the atomic heat of ice, were not at that time correctly known.

heat for greater distances from 0° , 8.6, and for temperatures nearer 0° , 9.1 to 9.2. The atomic heats have been found—

		For H_2O .
For $BaCl_2 \cdot 2H_2O$, § 84.....	41.7	
„ the chlorides, $R Cl_2$, § 84.....	M 18.5	
	<hr/>	
Remains for $2H_2O$	23.2	11.6
„ $CaCl_2 \cdot 6H_2O$, § 84.....	75.6	
„ the chlorides, $R Cl_2$, § 84.....	M 18.5	
	<hr/>	
Remains for $6H_2O$	57.1	9.5
„ Brucite, $MgO \cdot H_2O$, § 85.....	18.1	
„ the oxides, RO , § 85.....	M 11.1	
	<hr/>	
Remains for H_2O	7.0	7.0
„ diopside, $CuSiO_3 \cdot H_2O$, § 86.....	28.7	
„ the silicates, $RSiO_3$, § 86.....	M 20.5	
	<hr/>	
Remains for H_2O	8.2	8.2
„ $Na_2B_4O_7 \cdot 10H_2O$, § 87.....	146.9	
„ $Na_2B_4O_7$, § 87.....	47.1	
	<hr/>	
Remains for $10 H_2O$..	99.8	10.0
„ gypsum, $CaSO_4 \cdot 2H_2O$, § 87	M 45.8	
„ the sulphates, RSO_4 , § 87.....	M 26.1	
	<hr/>	
Remains for $2H_2O$	19.7	9.9

The Tables in §§ 84 to 89 contain data for several such comparisons, which lead to the same result as the preceding—that the atomic heat of water contained in solid compounds may, by subtracting the atomic heat of the anhydrous solid from that of the hydrated solid compound, be obtained in sufficient approximation to the atomic heat deduced from the direct determination of the specific heat of ice. The deviations from each other and from the atomic heat of ice as directly determined, which these indirect determinations exhibit, are not to be wondered at, when it is considered that all uncertainties in the atomic heats, from whose difference the atomic heat of solid water is deduced, are concentrated upon this difference.

98. The view already expressed and defended (compare especially §§ 12 and 13), that atoms and atomic groups are contained

in solid compounds with the same atomic heat that they have in the free state, is opposed to the view which has also been frequently expressed and defended—that the atomic heat of an element may in certain compounds differ from what it is in the free state, and may be different in different compounds. This view, and the reasons which may possibly be urged in its favour, must here be discussed.

The first statement of this view (compare § 6) simply goes to assert that the atomic heats of compounds may be calculated in accordance with the values resulting from the determinations of the specific heat, assuming that one constituent of the compound has the same atomic heat as in the free state, the other an altered one. What alteration is to be assumed depends merely on what assumption adequately satisfies the observed specific heat of the compound. The accuracy of the assumption is susceptible of no further control; the assumption itself cannot be regarded as an explanation of the observed atomic heat of the compound. And nothing is altered in this by assuming (compare §§ 6 and 11) that the changes in the atomic heat of a substance on entering into chemical compounds take place in more or less simple ratios.

A greater degree of probability must be granted to the view (compare § 10) that the atomic heats of the constituents of compounds, and the differences in the atomic heats of these bodies, according as they are combined or in the free state, depend upon the state of condensation in which these bodies are contained. If, for instance, from a consideration of the specific gravities or specific volumes (the quotient of the specific weights into the atomic weights) of compounds and of their constituents, a conclusion could be drawn with some degree of certainty as to the state of condensation in which the latter are present in the former, and if definite rules could be given for the variations of the atomic heats with the state of condensation, the result of such an investigation, if it agreed with the observed results for the atomic heats of compounds, might be called an explanation of these observations. But what is here presupposed is partially not attained and partially not attempted. And, moreover, as far as can be judged from individual cases, the same element, when present in different states of condensation, appears to have the same atomic heat. It has been attempted to deduce the state of condensation, or the specific volume, of oxygen in its compounds with heavy metals, by subtracting from the specific volume of the oxide

that of the metal in it, and considering the remainder as the volume of oxygen. It would follow from this that the specific volume of oxygen in cuprous oxide is much greater (about four times as great) than in stannic oxide. But if the atomic heat of oxygen be deduced by subtracting from the atomic heat of the oxide that of the metal in it, it is found that the atomic heat of oxygen in cuprous oxide and in stannic oxide gives almost exactly the same number. Hence it does not seem that the state of condensation in which a constituent may be contained in a compound has any material influence on the atomic heat of this constituent.

99. From all that has been said in the foregoing paragraphs the following must be adhered to. (1) Each element in the solid state, and at a sufficient distance from its melting point, has *one* specific or atomic heat, which may indeed vary to a certain extent with physical conditions, different temperature, or density, for instance, but not so considerably as to be regarded in considering in what relations the specific heat stands to the atomic weight or composition; and (2) that each element has essentially the same specific or atomic heat in compounds as it has in the free state. On the basis of these two fundamental laws we may now investigate what atomic heats individual elements have in the solid free state and in compounds. According to these propositions, indirect deductions of the atomic heats of such elements as could not be investigated in the solid free state are admissible in this sense; that from the atomic heat of a compound containing such an element the atomic heat of everything else in the compound is subtracted, and the remainder considered as the expression for the atomic heat of that element. Such indirect determinations of the atomic heat of elements may be uncertain, partly because the atomic heat of the compounds is frequently not known with certainty, as is seen from the circumstance that analogous compounds, for which there is every reason to expect the same atomic heat, are found by experiment to have atomic heats not at all agreeing; but more especially because the entire relative uncertainty in the atomic heats for a compound, and for that which is to be subtracted from its composition, is concentrated upon a small number, the residue remaining in the deduction. But when such deductions are made, not merely for individual cases, but for different compounds, and for entire series of corresponding compounds, they may be considered sufficiently

trustworthy to make the speculations based upon them worthy of attention. Of course in indirectly deducing the atomic heat of an element, its simpler compounds, and those containing it in greatest quantity (measured by the number of atoms), promise the most trustworthy results.

100. For *silver, aluminium, arsenic, gold, bismuth, bromine, cadmium, cobalt, copper, iron, mercury, iodine, iridium, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, osmium, lead, palladium, platinum, rhodium, antimony, selenium, tin, tellurium, thallium, tungsten, and zinc*, it may be assumed, from the determinations of their specific heat in the solid state (§ 82), that their atomic heats, in accordance with Dulong and Petit's law, are approximately equal, the average being 6.4. I do not believe that all these elements have really the same atomic heat, but think that some of them will hereafter be considered as exceptions to the above-mentioned law, as it will in the sequel be proved that several other elements have an atomic heat differing from 6.4. But for none of the previously mentioned elements are the present data, and the presumed deviation of the atomic heat from that of other elements, sufficient to justify their separation from them.

With the elements just mentioned *chlorine* must be associated from the close agreement of the corresponding chlorine, bromine, and iodine compounds (§ 84), and of the compounds KClO_3 , 24.8, and KAsO_3 , 25.3 (§ 88). To the atomic heats of these latter compounds those of individual salts, KNO_3 , approximate closely; the latter gave (§ 88) 21.8–24.4, mean 23.0, which, on the whole, agrees nearly enough with those found for the metallic oxides, R_2O_3 (§ 85). I count *nitrogen* also among the elements whose atomic heat may be assumed at 6.4, like that of most other elements, without, however, considering the determination of the atomic heat of this element as very trustworthy. To deduce the atomic heat of this element with certainty, compounds are wanting which contain, besides nitrogen, elements whose atomic heat has been directly determined. The fact that the atomic heat of the nitrates, $\text{R}_2\text{N}_2\text{O}_6$, was found (§ 88) in the mean to be 38.1, a third of which, 12.7, is somewhat less than the average atomic heat found for the oxides of heavy metals of the formula RO_2 , might be a reason for assigning to nitrogen a smaller atomic heat; while, on the other hand, the atomic heats of other nitrogen-compounds, in which, it is true, other elements

enter whose atomic heat is only indirectly determined, do not favour this view.

In the class of elements with the atomic heat about 6·4, *barium*, *calcium*, and *strontium* may be placed, from the agreement in the atomic heats of their compounds with the atomic heats of corresponding compounds of such elements as have been found by the direct determination of their specific heat in the free solid state to belong to that class (compare the atomic heats of the compounds HCl_2 in § 84, HCO_3 in § 86, HSO_4 in § 87, and HN_2O_6 in § 88); further, *rubidium* (compare the atomic heats of the compounds RCl in § 84, and R_2CO_3 in § 86); then also *chromium* (from the agreement in the atomic heats of Cr_2O_3 and Fe_2O_3 , § 84), and *titanium* (from the agreement in the atomic heats of TiO_2 and SrO_2 , § 84). To place *zirconium* in the same class has no other justification than that, on this assumption, the atomic heat of zircon may be calculated in accordance with that deduced from the observed specific heat of this mineral.

101. According to direct determinations of the specific heat, *sulphur* and *phosphorus* do not belong to this class. The more trustworthy determinations (for the sulphur the last two, for phosphorus the last three of the numbers in § 82) assign to these elements the atomic heat 5·4. That sulphur has a smaller atomic heat than the elements discussed in the last paragraphs, follows from the atomic heats of sulphur-compounds, compared with those of the corresponding compounds of such elements as have an atomic heat = 6·4. The average atomic heat of compounds RS and H_2S is 11·9, according to the determinations in § 83, while those of chlorine-compounds RCl and HCl (§ 84) = 12·8, that of the corresponding bromine-compounds = 13·9, and of the corresponding iodine-compounds = 13·4. In comparing more complicated sulphur-compounds, sulphates, for instance, with other compounds of analogous composition, the same is met with, although such complicated compounds are of little value in giving data for deciding on such small differences. The specific heat of the simpler phosphorus-compounds has not been investigated; for more complicated compounds, although they point to a smaller atomic heat for P than 6·4, the above remark also applies.

The determinations of the specific heat of *silicium* give for this element also a smaller atomic heat than 6·4 (compare § 82), and the same conclusion results from a comparison of the atomic heats of SiO_2 , and the oxides, H_2O_2 , of the silicates H_2SiO_3 , and

the oxides R_2O_3 . The atomic heat to be assigned to silicium cannot as yet be settled with any degree of certainty. Direct determinations, varying considerably from each other, give a specific heat mostly greater than 4; while the numbers obtained indirectly, and themselves also not closely agreeing, are partly considerably smaller. If in the sequel, I put the atomic heat of silicium at 3.8, corresponding to the lowest number found for the specific heat of this element, I do so for want of other and more certain data. I consider this number as quite uncertain.

The atomic heat of *boron*, from the direct determinations of the specific heat, is considerably smaller than 6.4; and the atomic heats of boron-compounds confirm this conclusion, as was discussed in §§ 93 and 95. By comparing the atomic heats of such boron and sulphur-compounds as contain, along with boron and sulphur, the same elements in the same proportions, the atomic heat of boron is found to be half that of sulphur. The atomic heat of $\text{KBO}_2 = 16.8$ is exactly half that found for $\text{K}_2\text{SO}_4 = 33.6$; the atomic heat of $\text{PbB}_2\text{O}_4 = 26.5$ is almost exactly equal to that for $\text{PbSO}_4 = 25.7$. Taking the atomic heat of S, in accordance with the above discussion, at 5.4, that of B would be 2.7; the numbers obtained directly for the atomic heat of boron (§ 82) from the experiments on the specific heat of this element agree with sufficient accuracy. In the sequel I take the atomic heat of boron at 2.7. A smaller number is obtained in other comparisons; for instance, of the atomic heats of B_2O_3 and of the oxides R_2O_3 , or of the salts RBO_2 and the oxides R_2O_2 ; but in such indirect determinations of the atomic heat, where such small numbers are to be determined, as is here the case with the atomic heat of boron, the results are very uncertain, owing to the fact that the entire uncertainty in the atomic heats of the compounds, and in the assumption that the elements corresponding to boron in compounds of analogous composition have really the atomic heat = 6.4, is thrown on the final result.

Lastly, *carbon* also, from the direct determinations of its specific heat (§ 82), has a much smaller atomic heat than 6.4. The same result follows from a comparison of the atomic heats of carbon-compounds: the atomic heat of the carbonates, $\text{R}_2\text{CO}_3 = 28.4$ as the mean of the determinations in § 86, is much smaller than that of $\text{R}_2\text{O}_3 (= 3\text{RO})$, which is the mean of the numbers in § 85 = 33.3; the atomic heat of the carbonates $\text{RCO}_3 = 20.7$, as the mean of the determinations in § 86, is much smaller than

27.1, the number found for As_2O_3 , Bi_2O_3 , Cr_2O_3 , Fe_2O_3 , and Sb_2O_3 as the atomic heat of oxides R_2O_3 . I put the atomic heat of carbon at 1.8 for C, as deduced from the determination of the specific heat of its purest variety, diamond.

102. In the preceding paragraphs I have discussed the elements which, from the determinations of their specific heat in the solid free state, have a smaller atomic heat than about 6.4. There remain to be discussed a few elements whose atomic heats are also less than those of most other elements, but can only be deduced from those of their compounds.

To this category belong *hydrogen**, even if the indirect determination of its atomic heat in the solid state is liable to the uncertainty just discussed. The atomic heat of water, H_2O , is (§ 85) = 8.6, and smaller by 7 than that of suboxide of copper, Cu_2O , which was found in the mean to be 15.6; the atomic heat of hydrogen would thus be $\frac{7}{2} = 3.5$ less than that of the elements to which copper belongs, as regards its atomic heat; hence the former would be $6.4 - 3.5 = 2.9$. The atomic heat of chloride of ammonium, NH_4Cl , has been found to be 20.0 (§ 81); the subtraction of the atomic heats for $\text{N} + \text{Cl} = 6.4 + 6.4 = 12.8$, leaves 7.2 as the atomic heat of 4H, and therefore 1.7 for that of H. The atomic heat of nitrate of ammonia, $\text{N}_2\text{H}_4\text{O}_3$, is 36.4 (§ 88); subtracting therefrom as the atomic heat of $\text{N}_2 + \text{O}_3$, the number 27.1, which has previously been frequently mentioned as the atomic heat of oxides R_2O_3 , we have 9.3 as the atomic heat of 4H, that is 2.3 for that of H. I put in the sequel the atomic heat of *hydrogen* at 2.3.

That *oxygen* has a smaller atomic heat than 6.4, follows from the fact that the oxygen compounds of the metals have a considerably smaller atomic heat than the corresponding chlorides, iodides, or bromides. For instance, the atomic heat of the oxides RO is as the mean of the determinations in § 85 = 11.1, while that of the chlorides RCl and RCl (§ 81), is 12.8, that of the corresponding bromides 13.9, and of the corresponding iodides 13.4. That of the oxides, RO_2 , as the mean of the determinations in § 85, of MnO_2 , SnO_2 , and TiO_2 is 13.7, while that of

* L. Gmelin (Handbuch der Chemie, 4 Aufl., vol. i, pp. 216 and 222) ascribed to hydrogen the same capacity for heat as that of an equivalent quantity of lead or mercury ($\text{H} = 1$, $\text{Cu} = 31.7$, $\text{Hg} = 169$); Schröder (Pogg. Ann., vol. lviii, p. 279) and Cannizzaro (Il Nuovo Cimento, vol. vii, p. 342) ascribed to hydrogen the same atomic heat as that of most other elements ($\text{H} = 1$, $\text{Cl} = 35.5$, $\text{Cu} = 63.4$, $\text{Hg} = 200$).

the chlorides RCl_2 (§ 85) is 18.5, and of the iodides $\text{RI}_2 = 19.4$. Taking the atomic heat of the other elements, which are contained in the following compounds, at 6.4, the atomic heat of oxygen, as deduced from the atomic heat of the oxides RO (11.1 in the mean), is $= 4.7$; as deduced from the oxides R_2O_3 (27.1 as the mean of the oxides of this formula previously frequently mentioned), it is $= 4.8$; from the above oxides, RO_2 (13.7 in the mean), it is $= 3.7$; it is found (compare § 88) from KAsO_4 (25.3) to be 4.1; from $\text{Pb}_3\text{As}_2\text{O}_8$ (65.4) to be 4.2; from KClO_3 (24.8) to be 4.0; from KClO_4 (26.3) to be 3.4; from KMnO_4 (28.3) to be 3.9. In the sequel the round number 4 is taken for the atomic heat of O.

Fluorine appears, lastly, to have an atomic heat considerably smaller than 6.4. The atomic heat of fluoride of calcium, CaF_2 , has been found to be (§ 84) only 16.4, considerably smaller than the corresponding chlorides, bromides, and iodides. I put the atomic heat of fluorine at $\frac{16.4 - 6.4}{2} = 5$.

103. Taking, in accordance with what has just been said, the atomic heat which an element has in a solid compound,

At 6.4 for Ag, Al, As, Au, Ba, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, I, Ir, K, Li, Mg, Mn, Mo, N, Na, Ni, Os, Pb, Pd, Pt, Rb, Rh, Sb, Se, Sn, Sr, Te, Ti, Tl, W, Zn, and Zr,

At 5.4 for S and P, at 5 for F, 4 for O, 3.8 for Si, 2.7 for B, 2.3 for H, and 1.8 for C; and assuming that the atomic heat of a solid is given by the sum of the atomic heats of the elements in it, we obtain the atomic heats; and dividing them by the atomic weights, we obtain the specific heats, in sufficiently close agreement with the specific heats as obtained by direct determinations of this property.

In the following Table, I give for all compounds for which the specific heat has been determined in a trustworthy manner, the specific heat calculated on these assumptions, compared with the numbers found experimentally. This calculation and this comparison are given in the same order which was followed in the synopsis § 82 to 89, and I refer to the latter as regards special remarks on the determinations. To distinguish the observers, N. again stands for Neumann, R. Regnault, Kp. Kopp, Pr. Person, A. Alluard, and Pp. Pape.

Alloys. (Compare § 82.)

			Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat Observed.	
Bi Sn	328	12·8	0·0390	0·0400	R.
Bi Sn ₂	446	19·2	0·0430	0·0450	R.
Bi Sn ₂ Sb	568	25·6	0·0451	0·0462	R.
Bi Sn ₂ Sb Zn ₂	698·4	38·4	0·0550	0·0566	R.
Pb Sb	329	12·8	0·0389	0·0388	R.
Pb Sn	325	12·8	0·0394	0·0407	R.
Pb Sn ₂	443	19·2	0·0433	0·0451	R.

104. *Arsenides and Sulphides.* (Compare § 83.)

Co As ₂	208·8	19·2	0·0919	0·0920	N.		
Ag ₂ S	248	18·2	0·0734	0·0746	R.		
Co As S	166	18·2	0·110	0·107	N.		
Cu ₂ S	158·8	18·2	0·115	0·121	R.	0·120	Kp.
Fe As S	163	18·2	0·112	0·101	N.		
As S	107	11·8	0·110	0·111	N.		
Co S	90·8	11·8	0·130	0·125	R.		
Cu ₂ Fe ₂ S	91·7	11·8	0·129	0·129	N.	0·131	Kp.
Fe S	88	11·8	0·134	0·136	R.		
Hg S	232	11·8	0·0509	0·052	N.	0·0512	R. 0·0517 Kp.
Ni S	90·8	11·8	0·130	0·128	R.		
Pb S	239	11·8	0·0494	0·053	N.	0·0509	R. 0·0490 Kp.
Sn S	150	11·8	0·0783	0·0837	R.		
Zn S	97·2	11·8	0·121	0·115	N.	0·123	R. 0·120 Kp.
Fe ₇ S ₈	648	88·0	0·136	0·153	N.	0·160	R.
As ₂ S ₃	246	29·0	0·118	0·113	N.		
Bi ₂ S ₃	516	29·0	0·0562	0·060	R.		
Sb ₂ S ₃	340	29·0	0·0853	0·0907	N.	0·0840	R.
Fe S ₂	120	17·2	0·143	0·128-0·133	N. 0·130	R.	0·126 Kp.
Mo S ₂	160	17·2	0·107	0·107	N.	0·123	R.
Sn S ₂	182	17·2	0·0945	0·119	R.		

105. *Chlorides, Bromides, Iodides, and Fluorides.* (Compare § 84.)

Ag Cl	143·5	12·8	0·0892	0·0911	R.		
Cu Cl	98·9	12·8	0·129	0·138	R.		
Hg Cl	235·5	12·8	0·0543	0·0521	R.		
K Cl	74·6	12·8	0·172	0·173	R.	0·171	Kp.
Li Cl	42·5	12·8	0·301	0·282	R.		
Na Cl	58·5	12·8	0·219	0·214	R.	0·213-0·219	Kp.
Rb Cl	120·9	12·8	0·106	0·112	Kp.		
N H ₃ Cl	53·5	22·0	0·411	0·373	Kp.		
Ba Cl ₂	208	19·2	0·0923	0·0896	R.	0·0902	Kp.
Ca Cl ₂	111	19·2	0·173	0·164	R.		
Hg Cl ₂	271	19·2	0·0708	0·0689	R.	0·640	Kp.
Mg Cl ₂	95	19·2	0·202	0·195	R.	0·191	Kp.
Mn Cl ₂	126	19·2	0·152	0·143	R.		
Pb Cl ₂	278	19·2	0·0691	0·0664	R.		
Sn Cl ₂	189	19·2	0·102	0·102	R.		
Sr Cl ₂	158·6	19·2	0·121	0·120	R.		
Zn Cl ₂	136·2	19·2	0·141	0·136	R.		
Ba Cl ₂ · 2H ₂ O	244	36·4	0·149	0·171	Kp.		

			Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.					
Ca	Cl ₂ . 6H ₂ O	219	70.8	0.323	0.345	Pr.				
Zn	K ₂ Cl ₄	285.4	44.8	0.157	0.152	Kp.				
Pt	K ₂ Cl ₆	488.6	57.6	0.118	0.113	Kp.				
Sn	K ₂ Cl ₆	409.2	57.6	0.141	0.133	Kp.				
Cr ₂	Cl ₆	317.4	51.2	0.161	0.143	Kp.				
Ag	Br	188	12.8	0.0681	0.0739	R.				
K	Br	119.1	12.8	0.107	0.113	R.				
Na	Br	103	12.8	0.124	0.138	R.				
Pb	Br ₂	367	19.2	0.0523	0.0533	R.				
Ag	I	235	12.8	0.0545	0.0616	R.				
Cu	I	190.4	12.8	0.0672	0.0687	R.				
Hg	I	327	12.8	0.0391	0.0395	R.				
K	I	166.1	12.8	0.0771	0.0819	R.				
Na	I	150	12.8	0.0853	0.0868	R.				
Hg	I ₂	454	19.2	0.0423	0.0420	R.				
Pb	I ₂	461	19.2	0.0416	0.0247	R.				
Ca	Fl ₂	78	16.4	0.210	0.208	N.	0.215	R.	0.209	Kp.
Al	Na ₃ Fl ₆	210.4	55.6	0.264	0.238	Kp.				

106. *Oxides.* (Compare § 85.)

Cu ₂	O	142.8	16.8	0.118	0.107	N.	0.111	Kp.		
H ₂	O	18	8.6	0.178	0.480	Pr.	0.474	R.		
Cu	O	79.4	10.4	0.131	0.137	N.	0.142	R.	0.128	Kp.
Hg	O	216	10.4	0.0481	0.049	N.	0.052	R.	0.053	Kp.
Mg	O	40	10.4	0.260	0.276	N.	0.244	R.		
Mn	O	71	10.4	0.146	0.157	R.				
Ni	O	74.8	10.4	0.139	0.159	R.				
Pb	O	22.3	10.4	0.0466	0.0512	R.	0.0553	Kp.		
Zn	O	81.2	10.4	0.128	0.132	N.	0.125	R.		
Mg	O . H ₂ O	58	19.0	0.328	0.312	Kp.				
Fe ₃	O ₄	232	35.2	0.152	0.164	N.	0.168	R.	0.156	Kp.
Mg	Al ₂ O ₅	142.8	35.2	0.246	0.194	Kp.				
Mg $\frac{1}{2}$	Fe $\frac{1}{2}$ Cr $\frac{3}{2}$ Al $\frac{1}{2}$ O ₄	196	35.2	0.179	0.159	Kp.				
Al ₂	O ₃	102.8	24.8	0.241	0.197	N.	0.217	R.		
As ₂	O ₃	198	24.8	0.125	0.128	R.				
B ₂	O ₃	69.8	17.4	0.249	0.237	R.				
Bi ₂	O ₃	468	24.8	0.0530	0.0605	R.				
Cr ₂	O ₃	152.4	24.8	0.163	0.196	N.	0.180	R.	0.177	Kp.
Fe ₂	O ₃	160	24.8	0.155	0.169	N.	0.167	R.	0.154	Kp.
Fe $\frac{5}{4}$	Ti $\frac{3}{4}$ O ₃	155.5	24.8	0.160	0.176	N.	0.177	Kp.		
Sb ₂	O ₃	292	24.8	0.0849	0.0901	R.				
Mn ₂	O ₃ . H ₂ O	176	33.4	0.189	0.176	Kp.				
Mn	O ₂	87	14.4	0.166	0.159	Kp.				
Si	O ₂	60	11.8	0.197	0.188	N.	0.191	R.	0.186	Kp.
Si $\frac{1}{2}$	Zr $\frac{1}{2}$ O ₂	90.8	13.1	0.144	0.146	R.	0.132	Kp.		
Sn	O ₂	150	14.4	0.096	0.093	N.	0.093	R.	0.089	Kp.
Ti	O ₂	82	14.4	0.176	0.172	N.	0.171	R.	0.159	Kp.
Mo	O ₃	144	18.4	0.128	0.132	R.	0.154?	Kp.		
W	O ₃	232	18.4	0.0793	0.0798	R.	0.0894?	Kp.		

107. *Carbonates and Silicates.* (Compare § 86.)

K ₂	C O ₃	138.2	26.6	0.192	0.216	R.	0.206	Kp.		
Na	C O ₃	106	26.6	0.251	0.273	R.	0.246	Kp.		

			Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.				
Rb ₂ C O ₃	230.8	26.6	0.115	0.123	Kp.			
Ba C O ₃	197	20.2	0.103	0.108	N.	0.110	R.	
Ca C O ₃	100	20.2	0.202	0.203	N.	0.209	R.	0.205 Kp.
Ca ₁ Mg ₁ C O ₃	92	20.2	0.220	0.216	N.	0.218	R.	0.206 Kp.
Fe ₁ Mn ₁ Mg ₁ C O ₃	112.9	20.2	0.179	0.166	Kp.			
Mg ₁ Fe ₁ C O ₃	91.1	20.2	0.222	0.227	N.			
Pb C O ₃	267	20.2	0.0757	0.0814	N.	0.0791	Kp.	
Sr C O ₃	147.6	20.2	0.137	0.145	N.	0.145	R.	
Ca Si O ₃	116	22.2	0.191	0.178	Kp.			
Ca ₁ Mg ₁ Si O ₃	108	22.2	0.205	0.191	N.	0.186	Kp.	
Cu Si O ₃ . H ₂ O	157.4	30.8	0.195	0.182	Kp.			
Mg ₁ Fe ₁ Si O ₄	145.8	32.6	0.223	0.206	N.	0.189	Kp.	
Al ₂ K ₂ Si ₆ O ₁₆	557	112.4	0.202	0.191	N.	0.183	Kp.	
Al ₂ Na ₂ Si ₆ O ₁₆	524.8	112.4	0.214	0.196	N.	0.190	Kp.	

108. *Borates, Molybdates, Tungstates, Chromates and Sulphates.*
(Compare § 87.)

K B O ₂	82	17.1	0.209	0.205	R.			
Na B O ₂	65.9	17.1	0.260	0.257	R.			
Pb B ₂ O ₄	292.8	27.8	0.0949	0.0905	R.			
Pb B ₄ O ₇	362.6	45.2	0.124	0.114	R.			
K ₂ B ₄ O ₇	233.8	51.6	0.221	0.220	R.			
Na ₂ B ₄ O ₇	201.6	51.6	0.256	0.238	R.	0.229	Kp.	
Na ₂ B ₄ O ₇ . 10 H ₂ O	381.6	137.6	0.366	0.385	Kp.			
Pb Mo O ₄	367	28.8	0.0785	0.0827	Kp.			
Ca W O ₄	288	28.8	0.100	0.0967	Kp.			
Fe ₂ Mn ₃ W O ₄	303.4	28.8	0.0949	0.0978	R.	0.0930	Kp.	
Pb Cr O ₄	323.2	28.8	0.0891	0.0900	Kp.			
K ₂ Cr O ₄	194.4	35.2	0.181	0.185	R.	0.189	Kp.	
K ₂ Cr ₂ O ₇	294.6	53.6	0.182	0.189	R.	0.186	Kp.	
K H S O ₄	136.1	30.1	0.221	0.244	Kp.			
K ₂ S O ₄	174.2	34.2	0.196	0.190	R.	0.196	Kp.	
Na ₂ S O ₄	142	34.2	0.241	0.231	R.	0.227	Kp.	
N ₂ H ₈ S O ₄	132	52.6	0.398	0.350	Kp.			
Ba S O ₄	233	27.8	0.119	0.109	N.	0.113	R.	0.108 Kp.
Ca S O ₄	136	27.8	0.204	0.197	R.	0.185	N.	0.178 Kp.
Cu S O ₄	159.4	27.8	0.174	0.184	Pp.			
Mg S O ₄	120	27.8	0.232	0.222	R.	0.225	Pp.	
Mn S O ₄	151	27.8	0.184	0.182	Pp.			
Pb S O ₄	303	27.8	0.0917	0.0872	R.	0.0818	N.	0.0822 Kp.
Ir S O ₄	183.6	27.8	0.151	0.143	R.	0.136	N.	0.135 Kp.
Zn S O ₄	161.2	27.8	0.172	0.174	Pp.			
Cu S O ₄ . H ₂ O	177.4	36.4	0.205	0.202	Pp.			
Mg S O ₄ . H ₂ O	138	36.4	0.264	0.264	Pp.			
Zn S O ₄ . H ₂ O	179.2	36.4	0.203	0.202	Pp.			
Ca S O ₄ . 2 H ₂ O	172	45.0	0.262	0.273	N.	0.259	Kp.	
Cu S O ₄ . 2 H ₂ O	195.4	45.0	0.230	0.212	Pp.			
Zn S O ₄ . 2 H ₂ O	197.2	45.0	0.228	0.224	Pp.			
Fe S O ₄ . 3 H ₂ O	206	53.6	0.260	0.247	Pp.			
Cu S O ₄ . 5 H ₂ O	249.4	70.8	0.284	0.285	Kp.	0.316	Pp.	
Mu S O ₄ . 5 H ₂ O	241	70.8	0.294	0.323	Kp.	0.338	Pp.	
Ni S O ₄ . 6 H ₂ O	262.8	79.4	0.302	0.313	Kp.			
Co S O ₄ . 7 H ₂ O	280.8	88.0	0.313	0.343	Kp.			
Fe S O ₄ . 7 H ₂ O	278	88.0	0.317	0.346	Kp.	3.356	Pp.	

		Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.		
Mg	S O ₄ . 7 H ₂ O	..	246	88.0	0.358	0.362	Kp. 0.407 Pp.
Ni	S O ₄ . 7 H ₂ O	..	280.8	88.0	0.313	0.341	Pp.
Zn	S O ₄ . 7 H ₂ O	..	287.2	88.0	0.306	0.347	Kp. 0.328 Pp.
Mg	K ₂ S ₂ O ₈ . 6 H ₂ O	..	402.2	113.6	0.282	0.264	Kp.
Ni	K ₂ S ₂ O ₈ . 6 H ₂ O	..	437	113.6	0.260	0.245	Kp.
Zn	K ₂ S ₂ O ₈ . 6 H ₂ O	..	443.4	113.6	0.256	0.270	Kp.
Al ₂	K ₂ S ₄ O ₁₆ . 54 H ₂ O.	..	949	317.6	0.335	0.371	Kp.
Cr ₂	K ₂ S ₄ O ₁₆ . 24 H ₂ O.	..	998.6	317.6	3.318	0.324	Kp.

109. *Arseniates, Phosphates, Pyrophosphates, and Metaphosphates, Nitrates, Chlorates, Perchlorates, and Permanganates.* (Compare § 88.)

K	As O ₃	162.1	24.8	0.153	0.156	R.	
K	H ₂ As O ₄	180.1	33.4	0.185	0.175	Kp.	
Pb ₃	As ₂ O ₈	899	64.0	0.0712	0.0728	R.	
Ag ₃	P O ₄	419	40.6	0.0969	0.0896 ?	Kp.	
K	H ₂ P O ₄	136.1	32.4	0.238	0.208	Kp.	
Na ₂	H P O ₄ . 12 H ₂ O..	358	139.7	0.390	0.408	Pr.	
Pb ₃	P ₂ O ₈	811	62.0	0.0764	0.0798	R.	
K ₄	P ₂ O ₇	330.4	64.4	0.195	0.191	R.	
Na ₄	P ₂ O ₇	263	64.4	0.242	0.228	R.	
Pb ₂	P ₂ O ₇	588	51.6	0.0878	0.0821	R.	
Na	P O ₃	102	23.8	0.233	0.217	Kp.	
Cl	P ₂ O ₆	198	41.2	0.208	0.199	R.	
Ag	N O ₃	170	24.8	0.146	0.144	R.	
K	N O ₃	101.1	24.8	0.215	0.239	R.	0.230 Kp.
K $\frac{1}{2}$ Na $\frac{1}{2}$	N O ₃	93	24.8	0.267	0.235	Pr.	
Na	N O ₃	85	24.8	0.292	0.278	R.	0.257 Kp.
N ₂	H ₄ O ₃	80	34.0	0.425	0.455	Kp.	
Ba	N ₂ O ₆	261	43.2	0.166	0.152	R.	0.145 Kp.
Pb	N ₂ O ₆	331	43.2	0.130	0.110	Kp.	
Sr	N ₂ O ₆	211.6	43.2	0.204	0.181	Kp.	
K	Cl O ₃	122.6	24.8	0.202	0.210	R.	0.194 Kp.
Ba	Cl ₂ O ₆ . H ₂ O	322	51.8	0.161	0.157	Kp.	
K	Cl O ₄	138.6	28.8	0.208	0.190	Kp.	
K	Mn O ₄	158.1	28.8	0.182	0.179	Kp.	

110. *Organic Compounds.* (Compare § 89.)

			Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.	
Cyanide of mercury	Hg	C ₂ N ₂	252	22.8	0.091 0.100 Kp.
„ „ zinc and potassium	Zn	K ₂ C ₄ N ₄	247.4	52.0	0.210 0.241 Kp.
Ferrocyanide of potassium..	Fe	K ₃ C ₆ N ₆	329.3	74.8	0.227 0.233 Kp.
Ferricyanide of potassium..	Fe ₃	K ₄ C ₆ N ₆ . 3 H ₂ O	422.4	107.0	0.253 0.280 Kp.
Chloride of carbon.	C ₂	Cl ₆	237	42.0	0.177 0.178 Kp.
Naphthalene	C ₁₀	H ₈	128	36.4	0.284 0.310 A.

				Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.	
Cerotic acid	..	$C_{27} H_{54} O_2$..	410	108.8	0.441	0.429	Pr.
Palmitate of melis- syle	$C_{46} H_{92} O_2$..	676	302.4	0.447		
Cane-sugar	..	$C_{12} H_{22} O_{11}$..	342	116.2	0.340	0.301	Kp.
Mannite	..	$C_6 H_{14} O_6$..	182	67.0	0.368	0.324	Kp.
Succinic acid	..	$C_4 H_6 O_2$..	118	37.0	0.314	0.313	Kp.
Tartaric acid	..	$C_4 H_6 O_6$..	150	45.0	0.300	0.288	Kp.
Racemic acid	..	$C_2 H_6 O_6 \cdot H_2 O$..	168	53.6	0.319	0.319	Kp.
Formiate of barium..	..	$C_2 H_2 Ba O_4$..	227	30.6	0.135	3.143	Kp.
Oxalate of potassium.	..	$C_2 K_2 O_4 \cdot H_2 O$..	184.2	41.0	0.223	0.236	Kp.
Quadroxalate of pot- ass	$C_2 H_3 K O_8 \cdot 2 H O$..	254.1	69.7	0.274	0.283	Kp.
Bitartrate of potassium	..	$C_4 H_5 K O_6$..	188.1	49.1	0.261	0.257	Kp.
Seignette salt	..	$C_4 H_4 Na K O_6 \cdot 4 H_2 O$..	282.1	87.6	0.311	0.328	Kp.
Bimalate of potassium	..	$C_8 H_{10} Ca O_{10} \cdot 8 H_2 O$..	450	152.6	0.339	0.338	Kp.

111. The preceding synopsis shows, for the great majority of substances contained in it, an adequate agreement between the observed specific heats and those calculated on such simple assumptions. In estimating the differences, the extent must be remembered to which various observers differ for the same substance. It must be considered that the present better determinations of the specific heat, even those made by the same experimenter, for substances where it may be expected that Neumann's law applies, do not agree exactly with it, not more nearly than within $\frac{1}{10}$ or $\frac{1}{9}$ of the value; and that for those elements which are considered here as obeying Dulong and Petit's law, even greater deviations occur between the numbers found experimentally and those to be expected on the assumption of the universal validity of this law. (These deviations, *i.e.* the differences between the atomic heats found for these elements, are seen from § 82.) The extent to which the experimentally determined specific heats deviate from such a law, Neumann's for instance, in bodies for which calculation takes it as applying, gives, of course, the means of judging what differences may occur between the observed and calculated numbers without invalidating the admissibility of the calculation attempted. And it is as much a matter of course that, in those bodies in which a marked deviation from Neumann's law has been already mentioned (compare § 95), a greater difference is found in the present synopsis between calculation and observation.

I consider the agreement between calculation and observation,

as shown in the synopsis § 103 to 110, as in general sufficient for a first attempt of that kind. But it need scarcely be mentioned that I by no means consider the calculated as more accurate than the observed numbers, or among several numbers consider that the most accurate which is nearest the calculated; for that, the bases of calculation are much too uncertain. The list of atomic heats given at the commencement of § 103 is scarcely much more accurate than were the first tables of atomic weights; but just as the latter have experienced continual improvements, and thus what was at first only an approximate agreement between the calculated and observed composition of bodies, has been brought within considerably narrower limits, and apparent exceptions have been explained, so, in like manner, will this be the case for ascertaining what atomic heats are to be assigned to the elements, and how the atomic heats of compounds may be deduced therefrom. This much, however, may even now be said, that while formerly for many solid substances, a statement of the specific heat could in no way be controlled, a concealed source of error for the determination of this property was not indicated, and an error which materially altered the number for this property could not be recognised, at present, even if only roughly, such a control is possible. Compare § 77.

PART VI.—*Considerations on the Nature of the Chemical Elements.*

112. The proof given in the preceding that Dulong and Petit's law is not universally valid, justifies certain conclusions, in reference to the nature of the so-called chemical elements, which may here be developed.

What bodies are to be regarded as chemical elements? Does the mere fact of nondecomposibility determine this? or may a body be nondecomposable in point of fact, and yet, from reasons of analogy, be regarded, not as an element but as a compound? The history of chemistry furnishes numerous examples of cases in which sometimes one and sometimes another mode of view led to results which at present are regarded as accurate. The earths were in 1789 non-decomposable in point of fact, when Lavoisier expressed the opinion that they were compounds, oxides of unknown metals. Lavoisier's argumentation was based on the fact that the earths enter as bases into salts, and that it was to be assumed in regard

to all salts, that they contained an oxygen-acid and an oxygen-base. But the view, founded on the same basis, that common salt contains oxygen, and the subsequent view that what is now called chlorine contained a further quantity of oxygen besides the elements of an oxygen-acid, did not find an equally permanent recognition. On the basis of the actual nondecomposibility of chlorine, Davy, from about 1810, maintained its elementary character; and this view has become general, especially since Berzelius, after a long struggle against it, adopted it, more I think because he was out-voted than because he was convinced.

Almost all chemists of the present time consider chlorine, and in conformity therewith, bromine and iodine, as elementary bodies; but we know with what persistence Schönbein attacks this view, and adheres to the opinion that these bodies are oxygen-compounds, peroxides of unknown elements. Is there anything which enables us to decide with greater certainty on the elementary nature of chlorine and the analogous bodies than has hitherto been the case?

No one can maintain that the bodies which chemists regard as elements are absolutely simple substances. We are compelled to admit the possibility that they may be decomposed into still simpler bodies; how far a body is to be regarded as an element, is so far relative, that it depends on the development of the means of decomposition which practical chemistry has at its disposal, and on the trustworthiness of the conclusions which theoretical chemistry can deduce. A discussion as to whether chlorine or iodine is an elementary body can be taken only in the sense whether chlorine is as simple a body as oxygen or manganese, or nitrogen; or whether it is a compound body, as peroxide of manganese or peroxide of hydrogen for example.

If Dulong and Petit's law were universally valid, it would indicate, not merely for chemical elements a relation between the atomic weight and the specific heat in the solid state, but it could be used as a test for the elementary nature of a body whose atomic weight is known. That iodine, from a direct determination, and chlorine by an indirect determination of specific heat, had atomic heats agreeing with Dulong and Petit's law, would be a proof that iodine and chlorine, if compounds at all, are not more so than other so-called elements for which this law is regarded as valid.

According to Neumann's law, compounds of analogous atomic

composition have approximately the same atomic heats. In general, bodies whose atom consists of a relatively greater number of non-decomposable atoms, or is of more complicated composition, have greater atomic heats. In these compounds, more especially those whose elements all follow Dulong and Petit's law, magnitude of atomic heat is exactly a measure of the complexity or of the degree of composition (compare § 93). If Dulong and Petit's law were valid, it could be concluded with great positiveness that the so-called elements, if they are compounds of unknown and simpler substances, are compounds of the same order. It would be a remarkable result that the act of chemical decomposition had everywhere found its limit at such bodies as those which, if compound at all, have, with every difference of chemical deportment, the same degree of complexity. Imagine the simplest bodies, probably as yet unknown to us, the true chemical elements, forming a horizontal spreading layer, and piled above them, the simpler and then the more complicated compounds; the universal validity of Dulong and Petit's law would include the proof, that all elements at present assumed by chemists lay in the same layer, and that chemistry, in recognising hydrogen, oxygen, sulphur, chlorine, and the different metals as nondecomposable bodies, had penetrated to the same depth in that field of inquiry, and had found at the same depth the limit to its penetration.

This result I formerly propounded* when I still believed in the validity of Dulong and Petit's law. But with the proof that this law is not universally true, the conclusion to which this result leads loses its justification. Starting now from the elements recognised in chemistry, we must rather admit that the magnitude of the atomic heat of a body depends, not only on the number of elementary atoms contained in one atom of it, or on the complexity of the composition, but also on the atomic heat of the elementary atoms entering into its composition; it appears now possible that a decomposable body may have the same atomic heat as a non-decomposable one.

To assume in chlorine the presence of oxygen, and to consider it as analogous to peroxide of manganese, or in general to the peroxide of a bi-equivalent element†, is less in accordance with

* "Ueber die Verschiedenheit der Materie vom Standpunkt des Empirismus," eine academische Rede. Giessen, 1860; s. 15.

† I must not omit to mention that equivalent weights of iodine and peroxide of manganese have almost equal capacity for heat. As regards oxidizing action, 127 of

what is at present considered true in chemistry, than to consider it as the peroxide of a monoequivalent element, analogous to peroxide of hydrogen. It is remarkable that peroxide of hydrogen, in the solid state or in solid compounds, must have almost as great an atomic heat (for $\text{HO } 2\cdot3 + 4 = 6\cdot3$) as those elements which obey Dulong and Petit's law, and especially as iodine, bromine, and chlorine, according to the direct and to the indirect determination of their atomic heat: the same must be the case for the analogous peroxides of such still unknown elements as have an atomic heat as great as that of hydrogen. As far as may be judged from its specific heat, chlorine *may* be such a peroxide; but this consideration shows no necessity for assuming that it actually is so.

In a great number of cases, the atomic heat of compounds gives more or less accurately a measure for the degree of complexity of their composition.* And this is the case also with such compounds as are comparable in their chemical deportment with undecomposed bodies. If cyanogen or ammonium had not been decomposed, or could not be so with the means at present offered by chemistry, the greater atomic heats of their compounds, compared with those of analogous chlorine or potassium-compounds (compare § 96), and of cyanogen and ammonium as compared with chlorine and potassium, would indicate the more complex nature of those so-called compound radicals. The conclusion appears admissible that for the so-called elements the directly or indirectly ascertained atomic heats are a measure for the complexity of their composition. Carbon and hydrogen, for example, if not themselves simple bodies, are more so than silicium or oxygen; and still more complex compounds are the elements which are now considered as following Dulong and Petit's law; with the restriction, however, that for these also the atomic heats may be more accurately determined and differences proved in them

iodine corresponds to $43\cdot5$ peroxide of manganese; Regnault found the specific heat of the former = $0\cdot0541$; I found that of the latter = 159 ;

$$127 \times 0\cdot0541 = 6\cdot87; 43\cdot5 \times 0\cdot159 = 6\cdot92.$$

* The differences in the atomic heats of the elements are of course most distinctly seen in their free state, but in their analogous compounds these differences are the less prominent the more complex the compounds, that is, the greater the number of atoms of the same kind and the same atomic heat which are united to those elementary atoms whose atomic heat is assumed to be unequal. The difference in the atomic heats of C and As, for instance ($1\cdot8$ and $6\cdot4$), is relatively far greater than for CaCO_3 and KAsO_3 ($20\cdot2$ and $24\cdot8$).

which justify similar conclusions.* One might be tempted, by comparing atomic heats, to form an idea how the more complex of the present non-decomposable bodies might be composed of more simple ones, just as such a comparison has been shown to be possible for chlorine; but it is at once seen that to carry out such an attempt, the atomic heats of the elements, especially those which can only be indirectly determined, are not settled with adequate certainty.

It may appear surprising, or even improbable, that so-called elements which can replace each other in compounds, as, for instance, hydrogen and the metals, or which enter into compounds as isomorphous constituents, like silicium and tin, should possess unequal atomic heats and unequal complexity of composition. But this is not more surprising than that undecomposable bodies, and those which can be proved to be compound, as, for example, hydrogen and nitric peroxide, or potassium and ammonium, should replace one another, preserving the chemical character of the compounds, and even be contained as corresponding constituents in isomorphous compounds.

I have here expressed suppositions with reference to the nature of the so-called elements which appear to me based on trustworthy conclusions from well-proved principles. It is in the nature of the case that the certain basis of fact and of what can be empirically demonstrated must be left. It must also not be forgotten that these conclusions only allow something to be supposed as to which of the present non-decomposable bodies are more complex and which of simpler composition, and nothing as to the question what simpler substances may be contained in the more complex ones. The consideration of the atomic heats may indicate something as to the structure of a compound atom, but in general gives no clue as to the qualitative nature of the simpler substances used in the construction of the more complex atoms. But even if these suppositions are not free from uncertainty and imperfection, they appear worthy of attention in a subject which, for science, is still so much in darkness, as is the nature of the non-decomposable bodies.

* It is possible, for example, that certain non-decomposable bodies which only approximately obey Dulong and Petit's law, are analogous compounds of simpler substances of essentially different atomic heat: the approximate agreement of the atomic heats of such non-decomposable bodies would then depend on a reason similar to that which has been given for the atomic heats of CaCO_3 and KAsO_4 . (Compare the previous note.)

XXI.—On *Picric Ether*.

By H. MÜLLER, Ph.D., and J. STENHOUSE, LL.D., F.R.S.

PROFESSOR MITSCHERLICH* believed that he had produced this compound by digesting for some hours a solution of picric acid in absolute alcohol mixed with a little sulphuric acid. This experiment has been repeated by Erdmann and several other chemists, but without success, a quantity of resinified picric acid being the only product. This result agrees with the description that Mitscherlich gives of his product, but which he did not analyse.

Picric ether may, however, be readily produced by acting on picrate of silver with iodide of ethyl.

One of the most convenient ways of preparing picrate of silver is to add an excess of carbonate of silver to a hot solution of picric acid, and after boiling for a few minutes, filter the solution and leave it to cool, when the picrate crystallises out in beautiful shining yellow needles, united in radiated groups.

One part of this salt in a perfectly dry state is placed in a flask furnished with a long condensing tube, and five parts by weight of iodide of ethyl are then poured on it. By using this large excess of iodide of ethyl, viz., ten times the theoretical quantity, the liquid does not become very hot, thus avoiding the loss of iodide of ethyl which takes place if equal weights are used, the action then being very violent. After allowing it to stand for a short time, it is digested in a water-bath for five or ten minutes to complete the decomposition, and the digesting tube being then replaced by a short bent one, the excess of iodide of ethyl is distilled off.

To the residue in the flask, consisting of iodide of silver and picrate of ethyl, 8 parts of spirit are added, and the whole is boiled for a few minutes and filtered; on cooling, the solution deposits the picric ether in long needles. By again treating the residue with spirit, a further amount of the ether may be extracted. The entire product is recrystallised once or twice from spirit and well washed with distilled water, in order to separate the small quantity of picric acid which adheres to it.

If an alcoholic solution of iodide of ethyl be used instead of the pure iodide in the preparation of picrate of ethyl, a large proportion of picric acid is set free, and at the same time some ethylic

* Lehrbuch. der Chemie i, 222.

ether is formed. In order to obtain the picric ether from this mixture, the solution is filtered from the iodide of silver, and, after evaporation, boiled with water, into which enough carbonate of calcium is gradually introduced to saturate the free picric acid. The picric ether separates in the form of a heavy oil, which congeals on cooling, and may be purified in the way already described. The first process already given is, however, by far the best.

Picric ether, when purified in the way described, consists of nearly colourless needles, having only a slight yellow tinge, which, when slowly deposited from spirituous solutions, are readily obtained one or two inches in length. When exposed to light they gradually become coloured. It is slightly soluble in boiling water, from which it crystallises out entirely on cooling. It is likewise soluble in iodide of ethyl, ether, bisulphide of carbon, and benzol. It melts at $78^{\circ}\cdot5$ C., and congeals at 73° C. When heated on platinum foil, it burns with a smoky flame. But when heated in a tube, it melts, and, on increasing the heat, is decomposed, with slight deflagration and deposition of carbon.

The substance dried in vacuo was analysed with the following results:—

I. $\cdot410$ gramm. gave $\cdot561$ gramm. carbonic acid, and $\cdot120$ gramm. water.
 II. $\cdot535$ „ „ $\cdot733$ „ „ $\cdot133$ „ „

	Theory.	I.	II.	Mean.
C ₈	37·36	37·33	37·37	37·35
H ₇	2·72	2·76	3·18	2·97
N ₃	16·34	—	—	—
O ₇	43·58	—	—	—

These numbers, as may be observed, agree very closely with the formula $C_6N_3O_7H_2\cdot C_2H_5$.

XXII.—*Styphnic or Oxypicric Ether.*

By JOHN STENHOUSE, LL.D., F.R.S.

THE styphnic acid which I employed for the preparation of this compound was obtained by treating with nitric acid the concentrated extract of sapan wood, which is largely manufactured for the use of calico printers. In preparing the acid from sapan

wood extract, I have found the following to be the best mode of proceeding.

20 measures of nitric acid, of sp. gr. 1.36, are heated in a large retort connected with a good condensing arrangement, 120 parts of the concentrated aqueous extract are gradually added, and the whole is digested for three or four hours, pouring back the weak acid that distils over.

The yellow solution thus obtained is first evaporated down over a bare flame, and then over a water-bath, until it becomes of the consistence of a thick syrup.

This syrup is gradually added to 4 measures of nitric acid, sp. gr. 1.45, previously heated to the boiling-point in a retort, 4 parts more acid being used to wash out the evaporating dish; the whole is then digested for four or five hours; about 3 parts of the acid are distilled off; the residue in the retort is transferred to a beaker, the retort being washed out with a little cold water (about 4 parts); the liquor is decanted from the sandy styphnic acid; 4 parts more water are added; the whole is well stirred; the liquid again decanted, and the crude styphnic acid is thrown upon a filter to drain. The washings, when evaporated over the water-bath and again digested with nitric acid, yield a small additional quantity of styphnic acid.

The crude styphnic acid obtained by the above process is placed in a flask with about 16 parts water, and, when boiling, a concentrated solution of carbonate of potassium is gradually added. When about one-half the proper quantity of carbonate of potassium solution has been poured in, the styphnic acid dissolves completely, but on the addition of more of the solution, a considerable quantity of styphnate of potassium is precipitated. As soon as it exhibits a decidedly alkaline reaction, the whole is boiled for a few minutes and allowed to cool, when the styphnate of potassium crystallises out. This is thrown on a filter and washed with a small quantity of cold water. After one or two recrystallisations, the potassium-salt is obtained in a perfectly pure state.

By treating a hot solution of the potassium-salt with nitric acid, perfectly pure styphnic acid may readily be procured.

Action of Chlorine on Styphnic Acid.

When styphnic acid is added to a *cold* solution of hypochlorite of calcium, chloropierin is evolved. In this respect it closely resembles picric acid; but on the application of heat, the whole

of the styphnic acid is decomposed, chloropierin and carbonic acid being the sole products.

When styphnic acid is heated for some time with hydrochloric acid and chlorate of potassium, it is completely decomposed, yielding chloropierin, but not a trace of chloranil. When picric acid is similarly treated, it produces, as is well known, both chloranil and chloropierin.

As styphnic acid, therefore, is incapable of yielding chloranil, and as the products of the action of reducing agents are so different from those of picric acid, styphnic acid is not, as Erdmann erroneously supposed, merely oxidated picric acid, but it must have a different nucleus entirely unconnected with that of picric acid.

Styphnic Ether.

The styphnate of silver used in the preparation of this ether was obtained from the potassium-salt, by dissolving it in about 20 to 25 parts of hot water, and precipitating by a slight excess of nitrate of silver, washing well with cold water, in which it is but slightly soluble, and drying at a moderate temperature. The styphnate of silver thus obtained is placed in a flask furnished with a long condensing tube, and 5 parts of iodide of ethyl are poured on it; the reaction is completed by heating it for five to ten minutes in a water-bath. When cold, the condensing tube is replaced by a short bent one and the excess of iodide of ethyl is distilled off. The residue is then treated with hot spirit, which extracts the styphnic ether and deposits it on cooling in large crystals. After two or three recrystallisations out of hot spirit, it is obtained in a state of perfect purity. This ether crystallises in the form of long laminae, which are nearly colourless when first prepared, but rapidly become orange-brown on exposure to light. It melts at $120^{\circ}5$, and when exposed to a higher temperature, volatilizes, but at the same time undergoes partial decomposition. When heated on platinum-foil, it burns with a bright flame, but without deflagration. It is soluble in alcohol and ether, and still more so in benzol, slightly soluble in bisulphide of carbon, and insoluble in water. When heated with solution of potash, it is decomposed, with production of styphnate of potassium and alcohol.

The following are the results of the analysis of the substance dried in vacuo :—

I. .436 grms. substance gave .637 grms. carbonic acid, and .146 grms. water.

II. .354 grms. substance gave .517 grms. carbonic acid, and .121 grms. water.

		Theory.	I.	II.	Mean.
C ₁₀	120	39·87	39·85	39·84	39·85
H ₁₁	11	3·66	3·72	3·80	3·76
N ₃	42	13·95	—	—	—
O ₈	128	42·52	—	—	—
	<hr/> 301	<hr/> 100·00			

This agrees remarkably well with the formula $\left. \begin{matrix} \text{C}_6\text{N}_3\text{O}_6\text{H} \\ 2\text{C}_2\text{H}_5 \end{matrix} \right\} \text{O}_2$.

Chrysammic Ether.

I have likewise obtained chrysammic ether by treating chrysammate of silver with iodide of ethyl. It crystallises in needles. I hope shortly to publish the analysis and description of this substance. The analyses were made for me by my assistant, Mr. Charles Edward Groves.

XXIII.—*The Water Supply of the Metropolis during the Year 1865–66.*

By E. FRANKLAND, F.R.S.

[Abstracted from the Annual Report to the Registrar-General.]

THE following are the results obtained in the monthly analyses of the metropolitan waters, during the year commencing February, 1865, and ending January, 1866* :—

The analytical determinations are conducted as follows :—1000 cubic centimetres of the water are evaporated in a weighed platinum dish on the water-bath, an accurately measured quantity of a solution of sodic carbonate of known strength having been previously added. The solution used contains 10 grammes of pure

* The analyses in the early part of the year were made by Dr. A. W. Hofmann.

dry sodic carbonate in one litre of water, and the quantity employed for one litre of the water under examination is 10 c.c., or .1 gramme of sodic carbonate.

The evaporation having been completed, the dish is transferred to an oil-bath, where it is exposed to a temperature of 120° — 130° C. (218° — 266° F.); it is then allowed to cool under a desiccator and weighed as quickly as possible, again exposed to the same temperature as before for about half an hour, and these operations are continued until the weight is constant. The weight of the dish and of the sodic carbonate added, being subtracted from that thus ascertained, the amount of solid residue in the quantity of water employed is obtained.

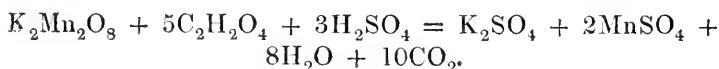
The dish containing the residue is now carefully ignited, and maintained at a dull red heat, until the organic matter has been burnt off. It is then allowed to cool, and a saturated aqueous solution of carbonic acid added, in quantity varying, of course, according to the amount of calcic and magnesian carbonates present, which is previously determined with sufficient accuracy by means of the soap-test; every decigramme of calcic carbonate is supposed to require 20 c.c. of carbonic acid water.

When sufficient carbonic acid has been added, the dish is dried at the same temperature as before until its weight is constant. The difference between this last weight and that before ignition represents the amount of organic and other volatile matter in the quantity of water employed. The next step has for its object the determination of the amount of oxygen necessary to oxidise the organic matter, and for this purpose a standard solution of potassic permanganate is used. This is prepared and applied in the following manner:—

$\frac{1}{200}$ th of the molecular weight of oxalic acid in grammes, viz., .6300 gramme of crystallised oxalic acid ($C_2H_2O_4.2aq.$) is accurately weighed out (after pressing between filter-paper), and dissolved in one litre of distilled water, which has been purified by re-distillation from potassic permanganate and sulphuric acid. About .4 gramme of potassic permanganate is now dissolved in another litre of water that has been similarly purified. A quantity of the oxalic acid solution (10 or 20 c.c.) is then accurately measured out into a large flask; the quantity of purified distilled water necessary to make it up to half a litre is added; and 15 c.c. of dilute sulphuric acid (1 vol. of acid to 5 of water) mixed with the whole. The permanganate is now added,

in small quantities at a time, from a burette furnished with a glass stop-cock, to the oxalic acid solution, care being taken to mix the liquids well after each addition. A portion of the mixed liquids is then poured into a glass cylinder 12 inches in height, and $1\frac{1}{2}$ inch in diameter, which is placed on a white surface. If, on looking down this column of liquid, a distinct pink coloration is visible at the expiration of ten minutes, the reaction is complete, and the number of c. c. of permanganate used is compared with the quantity of oxalic acid employed. The ratio of the two quantities having been observed, the strength of the permanganate solution is altered in such a manner that (as nearly as possible) n vols. of oxalic acid solution will require n vols. of permanganate solution to produce the above mentioned result. This experiment must now be repeated, and the strength of the permanganate altered, if necessary, until the desired result is obtained.

The following is the reaction which takes place in this experiment :—



One molecule of permanganate oxidises 5 molecules of acid, and, therefore, if the oxalic acid solution be of the strength of .63 gram. per litre (or .00063 gram. per c. c.), each c. c. of permanganate solution will contain .000316 gram. of pure potassic permanganate, as appears by the following calculation :—

Molecular weight of oxalic acid $\times 5$.		Molecular weight of potassic permanganate.		Amount of oxalic acid in 1 c. c.
630	:	316	: :	.000630 gram. : x .

x = amount of pure permanganate in 1 c. c. = .000316 gram.

This amount of permanganate represents .00008 gramme of available oxygen, as the following calculation shows :—

Molecular weight of potassic permanganate.	Atomic weight of oxygen $\times 5$.	Amount of permanganate in 1 c. c.
316	80	.000316 gram. : x .

x = .00008 gram. = amount of oxygen in 1 c. c.

A Measured quantity of the water to be analysed is now taken (half a litre is a convenient quantity), and 15 c. c. of dilute sulphuric acid (of the same strength as that used in standardizing

the potassic permanganate solution) having been mixed with it, the solution of permanganate is slowly added (exactly as in the experiment described above), until a pink coloration remains after the lapse of ten minutes. If the turbidity of the water, or the products of the oxidation of the organic matter contained in it, render the pink coloration undecided, a fresh experiment is made with 250 c.c. of the water, diluted with an equal quantity of purified distilled water. Should the amount of organic matter be small (requiring less than 1 c.c. of the permanganate), a litre of the water is used.

The number of c.c. of permanganate used is read off, and multiplied by the number that expresses what aliquot part of a litre of the analysed water was employed. The number thus obtained is now multiplied by $\cdot 00008$ (amount of oxygen in 1 c.c.), and we then have the amount of oxygen necessary to oxidise the organic matter in a litre of the water.

The above experiments are best performed by daylight.

The last operation consists in the application of Clark's soap-test, which is performed in the ordinary manner. The *permanent* hardness is determined after boiling the water for half an hour.

The results contained in the tables marked A, B, C, D, will now be sufficiently intelligible. Table A contains the amount of solid matter left on evaporation, and desiccation at 120° — 130° C. (248° — 266° F.); Table B, the loss which this matter undergoes on incineration; Table C, the amount of oxygen required to oxidise the organic matter; and, lastly, Table D, the degrees of permanent, temporary, and total hardness. The results are recorded in 100,000 parts.

Thus:—In September, 1865, we find, on referring to table A, that 100,000 lbs. of Chelsea water contained 24.45 lbs. of solid matter, of which, we find, by Table B, that 1.20 lbs. was driven off by incineration; from Table C, we learn that $\cdot 0368$ lb. of oxygen was required to oxidise the organic matter, in the said quantity of Chelsea water; while from Table D, we find that 18.1 lbs. of the solid residue were calcic carbonate, or its equivalent of hardening salts, of which 12.4 lbs. were removed by boiling, and 5.7 lbs. remained.*

* The degree of hardness hitherto employed by chemists is that first proposed by Dr. T. Clark, viz., one grain of calcic carbonate, or its equivalent, in one imperial gallon of water. The degrees in the above table are readily converted into Clark's degrees by multiplying by 7.

The tables may also be read (a) in the French method, *i. e.*, milligrams per kilogram, or litre, and (b) in the English method, *i. e.*, grains per gallon. As to the first method:—by moving the decimal point one place to the right, the above figures express in milligrams the quantities contained in one kilogram of the several waters. As to the second method:—A gallon of water weighs 10 lbs., and the amount of each constituent in grains per gallon is at once found by multiplying the numbers in the tables by $\cdot 7$. Thus, in September, 1865, a gallon of Chelsea water contained 17·115 ($= 24\cdot 45 \times \cdot 7$) grains of solid residuc.

I have also drawn out four additional tables marked respectively E, F₍₁₎, F₍₂₎, and G.

In these tables, the horizontal lines, on the left of which figures are placed, represent the respective number of parts of the constituent mentioned at the head of each table contained in (or required for) 100,000 parts of the waters. The spaces between the perpendicular lines represent the respective months the names of which appear at the head of the table.

The various curves against which the names of the Water Companies appear, represent, in the waters delivered by those companies, the monthly variation in the amount of the constituent mentioned at the head of each table, and also the amount of such constituent at any given time of the year.

Thus, for example, we find, on referring to Table A, that the analysis of a sample of water supplied by the New River Company in February, 1865, showed that it contained 29·60 parts of solid matter in 100,000 parts of the water; a reference to the records of the analysis (not given in the monthly tables) shows that the water in question was collected on February, 24. Accordingly these three facts are represented by the line marked “New River,” commencing rather above midway between 29 and 30 on Table E, at a position in the space representing February corresponding to the above date.

The points belonging to the other months are determined in a similar manner.*

An inspection of the curves drawn in these tables shows that river waters—viz. those supplied by the Thames, New River, and East London (River Lea) Companies—are subject to variations which occur but to a slight extent in the spring

* As the hardness of the waters was only estimated during the last five months of the year, the curves exhibiting its variation are omitted.

or artesian well waters delivered by the Kent and South Essex Companies.

The total solid matter contained in the former waters undergoes in all three cases a tolerably uniform diminution to the end of April; between which time and the end of May it suffers, in all cases, a sensible increase, after which it again diminishes to June and July. There is, then, a series of slight oscillations until November 1, when the curves make a sudden and enormous rise, which is tolerably well maintained until the end of the year.

It will also be found that the curves representing the variation in organic and other volatile matter, and in the oxygen required to oxidise the organic matter, take, in the case of the river waters, substantially the same form.

It is interesting to compare these curves with that representing the rain-fall during the same periods, given in Table H.

This comparison shows clearly (as might be anticipated) how closely the condition of river waters is connected with the amount of rain-fall; but, in opposition to the commonly received opinion, it proves that the waters in question are much purer in dry than in wet weather, even if the drought occurs during a very hot summer. Such, at all events, is the result of one year's observations; but it would obviously be premature to generalise upon the condition of the waters during a single year, which has been, moreover, in several respects, an exceptional one. For the same reason I will merely point out (without attempting to account for) the remarkable diminution in the amount of oxygen required to oxidise the organic matter of the river waters soon after the sudden rise due to the heavy rain-fall in October—the actual proportion of organic matter exhibiting no corresponding decrease.

The constituents of the well waters are, as above mentioned, subject to less variation than those of the river waters. To this rule however the organic matter contained in the former offers a notable exception. The curves of these waters representing the total solid residue and oxygen required to oxidise the organic matter (given in Tables E and G), give some indications of following the rain-fall curve, although those in Table F₍₂₎, representing the organic and other volatile matters, exhibit no such tendency.

TABLE A.
Solid Matter in 100,000 parts of the Waters.

Names of Water Companies.	1865.											1866.		Mean.
	Feb.	March.	April.	May.	June.	July.	August.	Sept.	Oct.	Nov.	Dec.	Jan.		
THAMES COMPANIES.														
Chelsea	31·72	29·47	26·62	26·60	24·43	23·58	23·75	24·45	23·67	24·98	28·00	30·12	26·44	
West Middlesex	30·63	30·16	26·70	25·70	24·27	22·42	23·22	23·75	24·16	25·30	28·91	32·02	26·43	
Southwark	32·62	30·14	26·79	27·33	24·63	22·76	23·68	25·45	18·78	29·32	31·32	29·90	26·89	
Grand Junction	32·11	29·85	26·58	27·85	24·95	22·94	23·18	24·50	24·56	26·99	29·51	30·70	26·97	
Lambeth.....	31·36	29·10	25·69	27·60	25·34	23·15	25·18	25·35	25·26	22·76	29·06	27·10	26·41	
OTHER COMPANIES.														
Kent	38·07	38·50	36·20	37·52	38·82	37·63	39·03	39·60	34·92	38·08	37·45	37·70	37·79	
New River	29·60	27·20	23·42	24·02	22·60	22·94	22·40	23·85	19·40	27·59	30·02	29·92	25·24	
East London	34·62	32·70	25·57	27·40	22·59	22·17	22·50	25·70	24·32	29·14	33·90	35·15	27·98	
South Essex	43·36	42·36	42·40	38·50	40·19	41·25	40·69	37·75	37·68	40·54	38·10	40·59	40·28	
Columns.....	1	2	3	4	5	6	7	8	9	10	11	12	13	

TABLE B.
Organic and other Volatile Matter in 100,000 parts of the Waters.

Names of Water Companies.	1865.												1866.	Mean.
	Feb.	March.	April.	May.	June.	July.	August.	Sept.	Oct.	Nov.	Dec.	Jan.		
THAMES COMPANIES.														
Chelsea	3·05	2·05	1·33	2·02	1·10	0·93	0·87	1·20	0·72	1·83	1·52	1·44	1·50	
West Middlesex	3·07	2·20	1·46	1·45	1·50	0·96	1·08	1·00	0·97	1·96	1·49	1·80	1·57	
Southwark	3·40	2·45	1·65	1·70	1·40	1·16	1·18	1·40	0·84	2·32	1·98	1·85	1·77	
Grand Junction	2·72	2·27	1·30	1·90	1·37	0·85	1·12	0·95	0·81	1·67	1·91	1·65	1·54	
Lambeth	2·70	2·00	1·14	1·95	1·55	0·97	1·12	1·45	1·34	2·17	1·08	1·94	1·61	
OTHER COMPANIES.														
Kent	1·55	2·66	1·85	1·94	1·57	1·67	1·66	2·30	1·74	1·04	0·61	1·26	1·65	
New River	2·00	1·73	0·95	0·65	1·05	0·55	0·93	0·65	0·77	0·73	0·54	1·30	0·98	
East London	3·30	2·48	1·35	1·65	0·88	1·03	0·88	0·90	0·86	2·42	1·56	2·24	1·62	
South Essex	2·70	2·48	1·75	1·65	2·23	2·50	2·56	1·20	0·84	1·44	0·86	1·69	1·82	
Columns	1	2	3	4	5	6	7	8	9	10	11	12	13	

TABLE C.

Amount of Oxygen required to oxidise Organic Matter in 100,000 parts of the Waters.

Names of Water Companies.	1865.											1866.	Mean.
	Feb.	March.	April.	May.	June.	July.	August.	Sept.	Oct.	Nov.	Dec.	Jan.	
THAMES COMPANIES.													
Chelsea	·0856	·0328	·0456	·0760	·0576	·0480	0592	·0368	·0384	·1606	·1942	·1184	·0794
West Middlesex.....	·0812	·0448	·0400	·0551	·0528	·0560	·0576	·0336	·0304	·1076	·1045	·0336	·0581
Southwark	·0811	·0544	·0512	·0816	·0640	·0720	·0565	·0408	·0416	·1521	·1972	·0568	·0791
Grand Junction.....	·0776	·0384	·0504	·0508	·0480	·0480	·0464	·0352	·0400	·0943	·1722	·0627	·0636
Lambeth.....	·0840	·0488	·0512	·0680	·0720	·0700	·0688	·0392	·0720	·1950	·0842	·1288	·0818
OTHER COMPANIES.													
Kent.....	·0692	·0168	·0152	·0096	·0064	·0080	·0088	·0088	·0048	·0156	·0070	·0096	·0149
New River	·0496	·0248	·0204	·0184	·0264	·0192	·0208	·0152	·0096	·0421	·0396	·0152	·0251
East London	·0744	·0344	·0200	·0488	·0336	·0336	·0188	·0272	·0240	·1341	·1274	·0291	·0504
South Essex	·0084	·0160	·0112	·0104	·0080	·0160	·0052	·0096	·0048	·0140	·0112	·0096	·0103
Columns.....	1	2	3	4	5	6	7	8	9	10	11	12	13

TABLE D.

Degrees of Hardness.

One degree = one part of Ca^{CO_3} (or its equivalent) in 100,000 parts of the waters. The columns marked with the letter (a) show the degrees of "Permanent," those marked (β) of "Temporary," and those marked (γ) of "Total" hardness.

Names.	1865.												1866.			Mean.		
	September.			October.			November.			December.			January.					
	a.	β.	γ.	a.	β.	γ.	a.	β.	γ.	a.	β.	γ.	a.	β.	γ.	Perma- nent.	Tempo- rary.	Total.
THAMES COMPANIES.																		
Chelsea	5.7	12.4	18.1	4.5	12.0	16.5	6.7	7.8	14.5	7.0	9.1	16.1	5.5	15.9	21.4	5.88	11.44	17.32
West Middlesex	5.6	11.8	17.4	4.4	12.7	17.1	6.4	11.1	17.5	6.8	11.9	18.7	6.7	14.7	21.4	5.98	12.44	18.42
Southwark	5.1	12.7	17.8	3.5	12.9	16.4	8.2	9.5	17.7	7.4	11.5	18.9	6.2	14.0	20.2	6.08	12.12	18.20
Grand Junction	6.0	12.1	18.1	4.2	12.2	16.4	6.8	11.0	17.8	7.4	11.0	18.4	5.7	15.4	21.1	6.02	12.32	18.34
Lambeth	5.0	13.8	18.8	3.7	13.7	17.4	7.6	5.4	18.0	8.8	7.6	16.4	6.4	9.0	15.4	6.30	9.90	16.20
OTHER COMPANIES.																		
Kent	7.9	17.4	25.3	7.8	15.9	23.7	9.7	17.7	27.4	8.8	17.4	26.2	9.2	17.3	26.5	8.68	17.14	25.82
New River	4.1	13.7	17.8	3.4	13.8	17.2	5.5	15.6	21.1	7.0	14.1	21.1	5.7	18.0	23.7	5.14	15.04	20.18
East London	5.3	13.7	19.0	4.0	13.4	17.4	9.0	13.2	22.2	7.2	15.0	22.2	6.1	18.7	24.8	6.32	14.80	21.12
South Essex	6.7	17.7	24.4	6.1	15.0	21.1	8.2	18.3	26.5	5.8	19.0	24.8	7.8	17.9	25.7	6.92	17.58	24.50
Columns	1			2			3			4			5			6		

TABLE E.

SHOWING THE MONTHLY VARIATION IN THE AMOUNT OF
SOLID MATTER IN 100,000 PARTS.

1

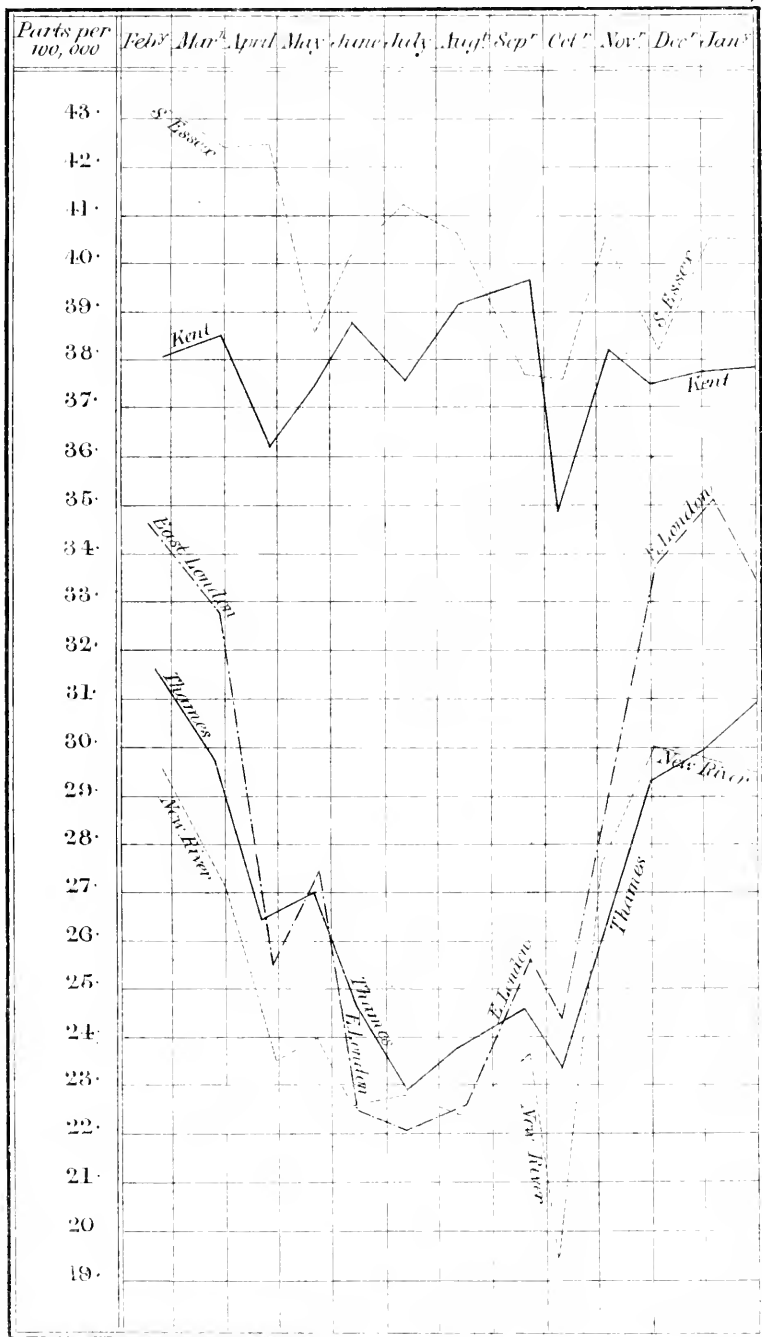


TABLE F (1)

SHOWING THE MONTHLY VARIATION IN THE AMOUNT OF ORGANIC
AND OTHER VOLATILE MATTER IN 100,000 PARTS
RIVER WATERS.

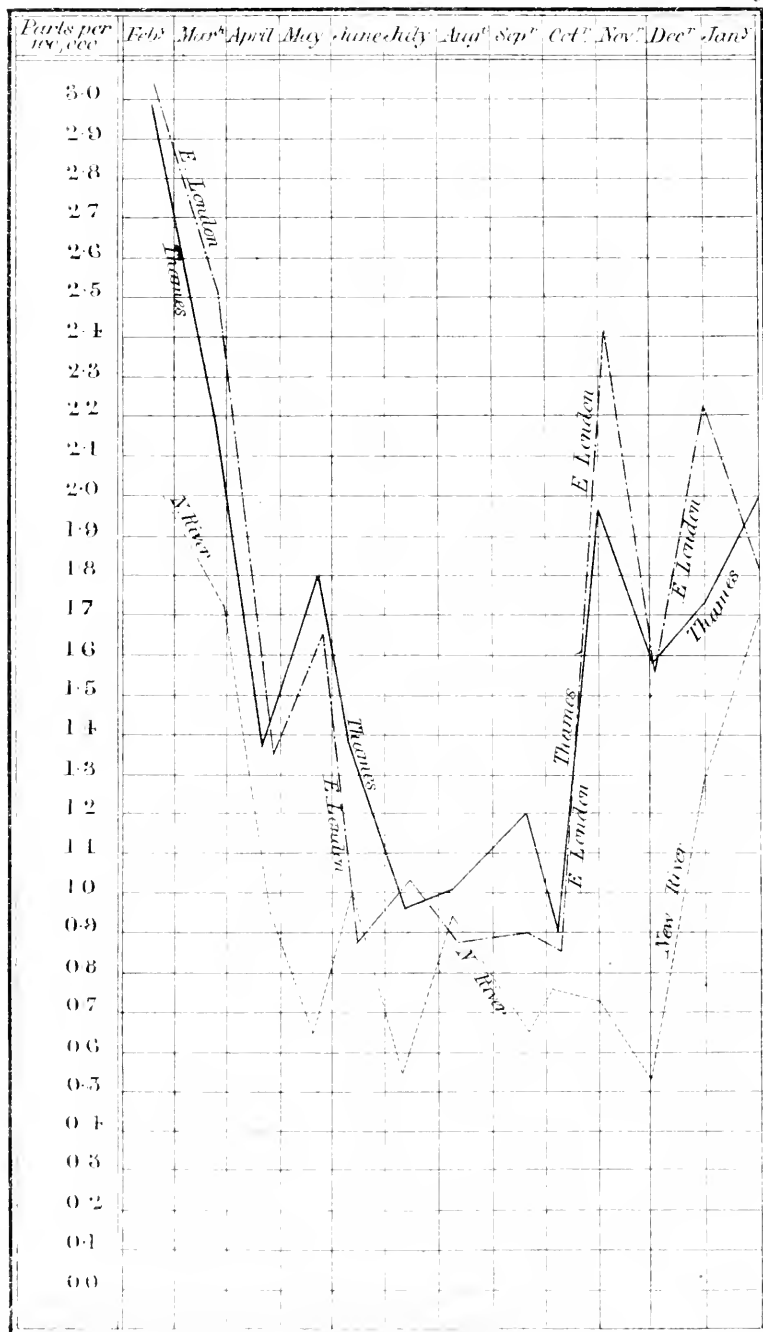


TABLE F (2)

SHOWING THE MONTHLY VARIATION IN THE AMOUNT OF ORGANIC
AND OTHER VOLATILE MATTER IN 100,000 PARTS.

WELL WATERS.

3

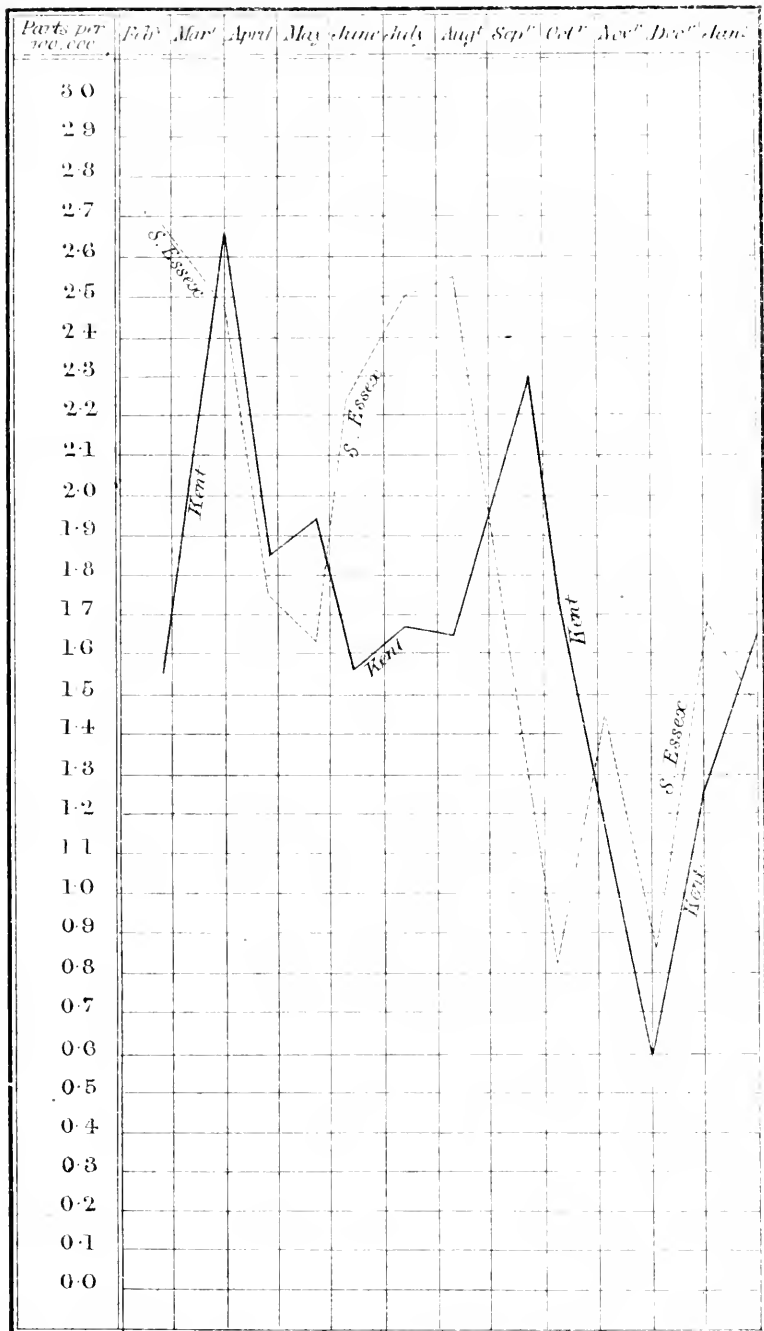


TABLE G.

SHOWING THE MONTHLY VARIATION IN THE AMOUNT OF
OXYGEN REQUIRED TO OXIDISE THE ORGANIC MATTER IN
100,000 PARTS.

4.

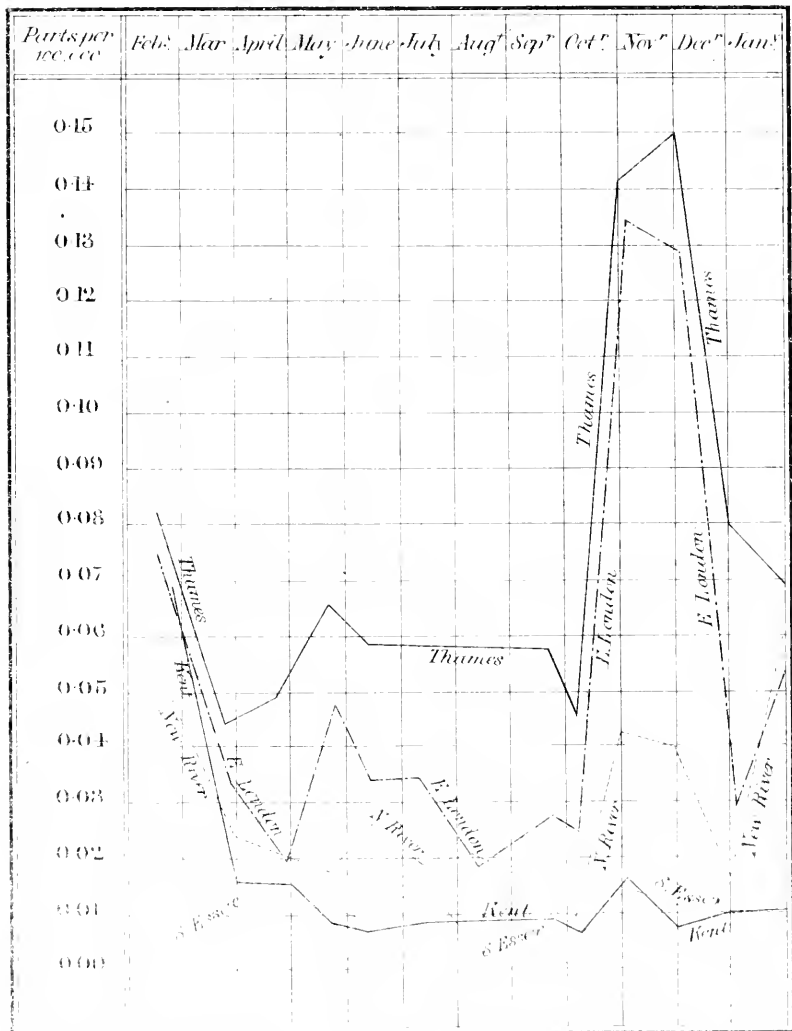
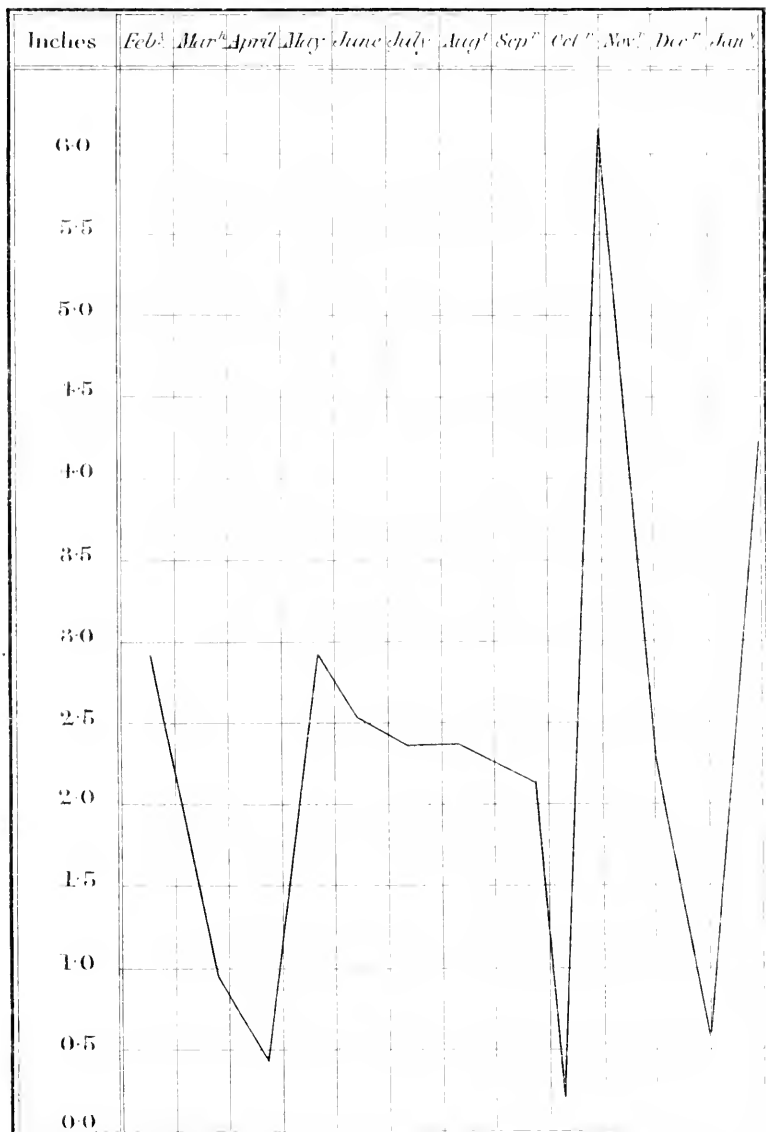


TABLE II.

SHEWING THE RAIN-FALL AT GREENWICH DURING
THE YEAR COMMENCING FEBRUARY 1865 & ENDING
JANUARY 1866.



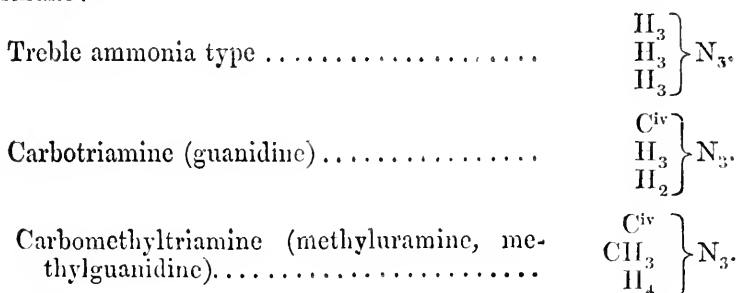
Drawn on 6th St. Martins Lane

XXIV.—*On the Synthesis of Guanidine.*

By A. W. HOFMANN, LL.D., F.R.S.

NEARLY twenty years ago,* when studying the action of chloride of cyanogen on aniline, I obtained a substance, melaniline, which, as to time, has become the starting-point of a very remarkable series of monacid triamines. Melaniline, originally regarded as a *diamine*, as cyandiphenyldiamine, may also be looked upon as constructed upon the type of three molecules of ammonia, held together by the presence of a quadrivalent carbon-atom, two atoms of hydrogen being at the same time replaced by phenyl; thus it appears in the light of a *triamine*, as carbodiphenyltriamine.

Melaniline was followed somewhat later by methyluramine, obtained by Dessaignes,† amongst other products, by the oxidation of creatine. To the same series belong, moreover, carbotriphenyltriamine‡ formed by the action of chloride of carbon on aniline, as well as the corresponding ethyl-compound, carbotriethyltriamine,§ which is generated by treating sodium-alcohol with cyanate or cyanurate of ethyl. But by far the most interesting term of this series, as to composition at all events, is undoubtedly the guanidine discovered by Prof. A. Strecker,|| when submitting guanine to the action of oxidizing agents: because in this compound the three ammonia-molecules are rivetted together by the carbon-atom without any hydrogen being replaced by atom-groups that could disguise its constitution. The relation of these bodies to the treble ammonia-type is evident by a glance at the following formulæ:—



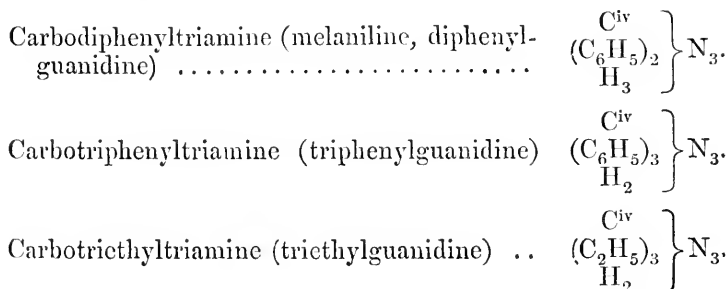
* Chem. Soc. Qu. J. i, 285.

† Ann. Ch. Pharm. xcii, 407.

‡ Proc. Roy. Soc. ix, 284.

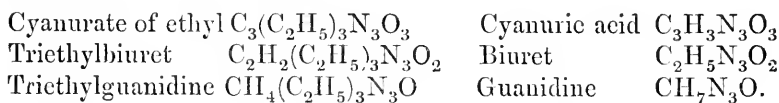
§ Proc. Roy. Soc. ix, 281.

Ann. Ch. Pharm. cxviii, 151.



The idea naturally suggested itself to prepare guanidine, which Strecker's beautiful researches have associated with some of the most interesting compounds, *mutatis mutandis*, by one of the methods used to procure the bodies which may be looked upon as guanidine derivatives.

In describing carbotriethyltriamine,* the body last mentioned in the preceding list, I have already called attention to the probability that guanidine might be obtained from cyanuric acid or biuret, just as the triethylated body is formed from cyanate of ethyl or its indifferent derivative (triethylbiuret), discovered by Habich and Limpricht.†



The correctness of this view has since been established by experiment, Finckh‡ having shown that biuret can, in fact, be converted into guanidine.

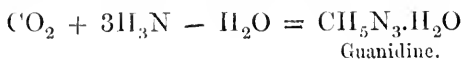
I have lately been engaged again in experiments on the formation of guanidine, in the course of which I have made some observations which I beg leave to communicate to the Chemical Society.

Guanidine, though first observed in a rather complicated process, is nevertheless of extremely simple constitution; it contains but one atom of carbon in its molecule, thus standing on the ill-defined boundary-line between the compounds of organic and inorganic nature. The molecule of guanidine contains the elements of one molecule of carbonic acid and three molecules of ammonia, *minus* one molecule of water.

* Loc. cit.

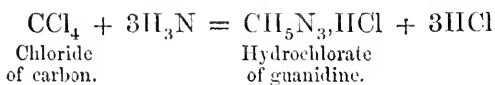
† Ann. Ch. Pharm. cix, 104.

‡ Ann. Ch. Pharm. cxxiv, 331.



Guanidine.

Nothing is easier than to split the molecule of guanidine, in accordance with the foregoing equation: in the presence of water it is easily converted into carbonic acid and ammonia. The prospect, on the other hand, of transforming carbonic acid and ammonia, with elimination of water, into guanidine was a less hopeful one. I have made indeed but few experiments in this direction, the action of chloride of carbon on ammonia promising a much more accessible result. Here it was possible to rely on unmistakeable analogies; the treatment of chloride of carbon with aniline, *i. e.*, phenylic ammonia, having yielded triphenylic guanidine, or carbotriphenyltriamine, the transformation of chloride of carbon by ammonia into guanidine, or carbotriamine, appeared all but a certainty:



Chloride
of carbon.

Hydrochlorate
of guanidine.

My expectations were not however realised by experiment. As yet I have not been able to obtain guanidine by submitting chloride of carbon to the action of ammonia. Although I have considerably varied the experiment, I have not hitherto observed the formation of guanidine in that reaction. If an aqueous solution of ammonia be treated with chloride of carbon, the reaction takes place only at a very high temperature, at which guanidine, if it be ephemerally formed, absorbs water, and is converted into carbonic acid and ammonia. If an alcoholic solution of ammonia be employed, the reaction takes place at a much lower temperature. After ten hours' digestion with alcoholic ammonia, every trace of chloride of carbon had disappeared; but the transformation is complicated, the elements of the alcohol participating in the reaction; brown resinous products are generated; and the formation of guanidine, which, it cannot be doubted, must take place when chloride of carbon and ammonia come in contact, under favourable circumstances, could not, in this case also, be proved by experiment.

The synthesis of guanidine succeeds, however, without difficulty if, instead of chloride of carbon, a substance very nearly related to it, the chloropierin* of Stenhouse, is made to act upon am-

* Chloropierin can be easily obtained on a large scale by the following process:—45.0 kilogrammes of freshly prepared bleaching powder, made into a paste with

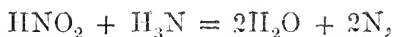
monia. Chloropierin may be regarded as tetrachloride of carbon in which one atom of chlorine is replaced by the atom group NO_2 ; accordingly there was reason to expect that the action of ammonia on it would give rise to a transformation perfectly analogous to that which theory had suggested in the case of chloride of carbon, with this difference, however, that in the reaction with chloropierin, there would be generated, together with hydrochlorate of guanidine, not three molecules of hydrochloric acid, but two molecules of hydrochloric acid and one molecule of nitrous acid.



Chloropierin.

Hydrochlorate of guanidine.

Chloropierin may be digested with aqueous ammonia at 100°C. for several days without undergoing any appreciable change. At a temperature between 150° and 160°C. , the reaction is completed in a few hours, and, indeed, exactly in accordance with the above equation. But the nitrous acid, when acted upon at that temperature by an excess of ammonia, undergoes the well-known transformation:—



and in consequence of the enormous pressure occasioned by the liberation of nitrogen, many of the tubes explode during the digestion. Those which have resisted the pressure must be opened with the greatest care before the blow-pipe, and even then often explode at the moment when the tube is blown out. In consequence of this inconvenience, I have endeavoured to facilitate the reaction by the addition of alcohol. A solution of chloropierin in alcoholic ammonia undergoes transformation even at 100°C. , the rapidity of the reaction depending upon the strength of the

water, are mixed with a solution of 4.5 kilogrammes of picric acid heated to 30°C. , the whole being rapidly stirred. The operation is performed in a comparatively large distilling apparatus of earthenware, which is surrounded by cold water and connected with a well-cooled worm. Powerful reaction soon sets in, the heat evolved causing the chloropierin which is formed to distil rapidly. In order to avoid the escape of uncondensed chloropierin into the laboratory, the receiver should be connected with a tube passing into the chimney. The first reaction being over, the water-bath in which the retort stands is heated to boiling, in order completely to drive over the remainder of the chloropierin. The yield of chloropierin is 114 per cent. of the picric acid employed.

It may here be stated that I have found the boiling point of chloropierin to be 112°C. , which is somewhat lower than that given by Dr. Stenhouse, who states it to be 120°C.

alcohol. The liquid acquires a yellow colour, and after forty-eight hours, crystals separate, which are easily recognized as chloride of ammonium. After cooling, the tubes are opened before the blow-pipe, to allow the nitrogen, which is liberated in small quantity even at this temperature, to escape. After six or eight days the action is complete. On now opening the tubes, the frightful odour of chloropierin is found to have disappeared, and the liquid can be mixed with water without separating into two layers.

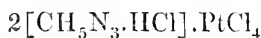
The strongly ammoniacal liquid, poured off from the copiously separated crystals of chloride of ammonium, contains, in addition to hydrochlorate of guanidine, a considerable quantity of chloride and nitrite of ammonium. This solution, on being acidulated with sulphuric acid, produces, in a mixture of starch and iodide of potassium, a deep blue coloration. To obtain the guanidine in the pure state, the liquid was evaporated on the water-bath, and the crystalline residue exhausted with absolute alcohol. A further quantity of chloride of ammonium remained undissolved, whilst the solution yielded upon evaporation, a deliquescent salt, the hydrochlorate of guanidine, in a nearly pure state.

To get rid of traces of ammonia, the base was liberated by oxide of silver, and left on the water-bath, or under the air-pump over sulphuric acid, until all the ammonia had disappeared. The strongly alkaline liquid, which quickly absorbed carbonic acid from the air, was then neutralised with hydrochloric acid, and precipitated with tetrachloride of platinum. The very soluble splendid ruby-red crystals, which were formed after some time, gave, on analysis, the following numbers:—

I. 1·3600 grm. of substance, dried at 100° C., gave 0·2214 grm. carbonic acid, and 0·2949 grm. water.

II. 0·6424 grm. of substance, dried at 100° C., gave 0·2400 grm. of platinum.

These numbers exactly accord with the formula,—

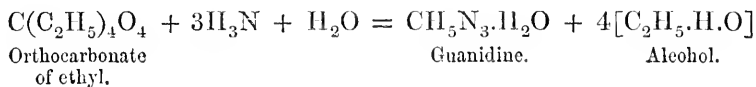


which requires the subjoined values,—

Theory.			Experiment.	
			I.	II.
C ₂	24	4.5	4.44	—
H ₁₂	12	2.3	2.40	—
N ₆	84	15.8	—	—
Pt	198	37.3	—	37.36
Cl ₆	213	40.1	—	—
	<hr/>	<hr/>		
	531	100.0		

I had hoped to be able to prepare in this way somewhat larger quantities of guanidine, which would lend itself to a great variety of interesting reactions. The slowness of the change, however, and the partial transformation of the nitrite of ammonium into gaseous products, renders the process difficult. The theoretical quantity of guanidine, moreover, is never obtained, a part of the newly formed substance being, by the assimilation of water, converted into carbonic acid and ammonia. After cooling, the upper part of the digesting tubes was invariably found to be coated with a thin film of carbonate of ammonium.

In order to avoid the evolution of nitrogen, I have prepared the interesting ether which Mr. Bassett* has obtained by acting with sodium on an alcoholic solution of chloropierin. This ether, happily called by Dr. Odling, *orthocarbonate of ethyl*, when acted upon by ammonia, was not less likely to be converted into guanidine.



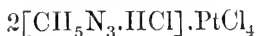
This view has been confirmed by experiment. At 100° C. orthocarbonate of ethyl and aqueous ammonia do not act upon one another, but at 150° C. transformation is accomplished in a short time. The clear solution yields upon evaporation a strongly alkaline substance, not volatile at 100°. After traces of ammonia had been expelled by exposure on the water-bath, hydrochloric acid and tetrachloride of platinum were added to the new base. The crystals which gradually separated had all the properties of the platinum-salt of guanidine, with which it was, moreover, identified by analysis.

* Chem. Soc. J. xvii, 198.

I. 0·6716 grm. of substance, dried at 100° C., and precipitated by sulphuretted hydrogen, &c., gave 0·2501 grm. of platinum.

II. 0·1920 grm. of substance, dried at 100° C., and analysed in the same way, yielded 0·0718 grm. of platinum.

These numbers agree very well with the formula—



	Theory.	Experiment.	
		I.	II.
Platinum percentages	37·4	37·24	37·3

But the yield in this case also is very small, guanidine when free being still more easily converted into carbonic acid and ammonia than when combined with acids. Taking, lastly, into consideration that the conversion of chloropicrin into orthocarbonate of ethyl is tedious and expensive, it is only too obvious that this process also cannot be recommended as a method for preparing guanidine on a large scale.

The production of guanidine from chloropicrin or orthocarbonate of ethyl may possibly lead to the examination of the action of ammonia upon the analogous compounds of other elements. A silicic ether corresponding to orthocarbonate of ethyl is well known :

Orthocarbonate of ethyl	$\text{C}(\text{C}_2\text{H}_5)_4\text{O}_4$
Orthosilicate of ethyl	$\text{Si}(\text{C}_2\text{H}_5)_4\text{O}_4$

Treated under favourable circumstances with ammonia, this body might be converted into *guanidine* containing *silicium*, in the place of carbon.

It deserves to be noticed that, according to the observations of Persoz*, the molecules of chloride of silicium and chloride of titanium are capable of fixing not less than six molecules of ammonia. The white compounds thus obtained, which are unfortunately decomposed by water, may be considered as mixtures of chloride of ammonium with hydrochlorate of guanidine containing silicium and titanium, to which respectively the names of *silicotriamine* and *titanotriamine* may be applied.

* Ann. Ch. Phys. xliv, 319.

XXV.—*On the Constitution of some Carbon-compounds.*

By HENRY DEBUS, Ph.D., F.R.S.

PART II.

At the end of the first part of this paper* it was pointed out that, according to our present experience, the group CH_2 , when it forms one of the proximate constituents of an organic compound consisting of carbon, hydrogen, and oxygen, does not combine with more than one atom of oxygen, producing the group CHH . Only one of the conclusions that may be deduced from this property will be considered in this place. If the theory advanced in my former communication† be accepted, and the property just alluded to is general, then it follows that no organic body can contain more oxygen-atoms than carbon-atoms, if an alcohol, and not more than $n + a$, if an acid of the basicity a with n carbon-atoms. This conclusion is in accordance with our present knowledge.

Methylic alcohol contains one atom of carbon and one of oxygen; formic acid is monobasic and contains one atom of carbon and two of oxygen. In glycol, we have two atoms of carbon and two of oxygen. Monobasic glycollic acid consists of two atoms of carbon, four atoms of hydrogen, and three of oxygen, whereas the bibasic oxalic acid contains two atoms of carbon and four of oxygen.

I have placed in Table I those compounds in which for n carbon-atoms the greatest number of oxygen atoms occur.

Substances with more than 7 atoms of carbon in each molecule contain fewer oxygen- than carbon-atoms. In general, it is observed that the number of oxygen-atoms increases with the number of carbon-atoms, but at a slower rate, and accordingly the ratio $\frac{\text{O}}{\text{C}}$ of oxygen- to carbon-atoms becomes smaller in more complex compounds.

The analogy which exists between the derivatives of ethylic hydride and those of propylic hydride leads to the conclusion that both groups possess a similar constitution.

* Chem. Soc. J. [2], iv, 30.

† Chem. Soc. J. [2], iv, 21, 22.

TABLE I.

Bodies of doubtful Composition are omitted.

Name.	Basicity.	Number of Carbon Atoms.	Number of Oxygen Atoms.
Methylic alcohol.....	..	1	1
Formic acid	Monobasic	1	2
Glycol	2	2
Oxalic acid	Bibasic	2	4
Glycerin	3	3
Mesoxalic acid	Bibasic	3	5
Erythrite	4	4
Tartaric acid	Bibasic	4	6
Amyl-glycol	5	2
Aposorbic acid	Bibasic	5	7
Desoxalic acid	Tribasic	5	8
Mannite, dulcite	6	6
Saccharic acid.....	Bibasic	6	8
Meconic acid	Tribasic	7	7

I propose to apply the theory, which has been advanced in the first part of this paper*, in the present communication to the carbon, hydrogen, and oxygen compounds, derived from propylic hydride.

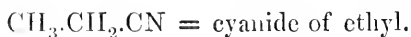
If we assume that propylic hydride will behave with chlorine like marsh-gas, propylic chloride, C_3H_7Cl , and hydrochloric acid ought to be obtained when the two bodies are placed in contact. The replacement of the chlorine in C_3H_7Cl , by the water-residue HO furnishes propylic alcohol, and the oxidation of the latter yields propionic aldehyde and propionic acid. The conversion of this acid into lactic acid may be accomplished by a well known process. The radical of malonic acid can be changed, in one of the urea-derivatives into that of mesoxalic acid, and this acid in its turn yields with nascent hydrogen, tartronic acid. The successive members of this group are the following :

Propylic hydride	C_3H_8
Propylic alcohol	C_3H_8O
Propionic aldehyde	C_3H_6O

* Chem. Soc. J. [2] iv, 21, 22.

Propionic acid	$C_3H_6O_2$
Lactic acid.....	$C_3H_6O_3$
Pyruvic acid.....	$C_3H_4O_3$ (?)
Malonic acid	$C_3H_4O_4$
Tartronic acid.....	$C_3H_4O_5$
Mesoxalic acid.....	$C_3H_2O_5$

The conversion of lactic acid into malonic acid has not yet been accomplished by experiment, but analogy justifies the conclusion that the two are related like glycollic and oxalic acids. The members of the propylic hydride group are thus connected in the same manner as those of the ethylic hydride group. The successive changes which the group C_3H_8 suffers in consequence of the gradual addition of oxygen are therefore the following:— 1, addition of 1 atom of oxygen; 2, loss of 2 atoms of hydrogen; 3, combination with one atom of oxygen,—propylic alcohol, propionic aldehyde and propionic acid being the results of the reactions. The repetition of these processes leads to lactic, pyruvic (?), and malonic acids. Tartronic acid again contains an atom of oxygen more than malonic acid, and mesoxalic acid 2 atoms of hydrogen less than the latter. Mesoxalic acid, however, cannot combine with an atom of oxygen without disintegration of its molecule. The eight atoms of hydrogen in propylic hydride arrange themselves accordingly in three groups; two groups, each consisting of 3 atoms of hydrogen, are replaced successively in the same manner by H^* and O, for one of the two remaining hydrogen-atoms the group H , or for both hydrogen-atoms 1 atom of oxygen may be substituted. These properties, in connection with the theory explained in my former paper,† lead to the formula $CH_3.CH_2.CH_3$ for propylic hydride. This expression is supported by the fact that we are able to build up some members of the propylic hydride group by uniting the groups which are supposed to be their proximate constituents. Propionic acid, according to Frankland and Kolbe's elegant reaction, may be formed from cyanide of ethyl.



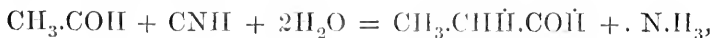
Replacing N by OH , we obtain propionic acid = $CH_3.CH_2.CO\dot{H}$
Ethylic hydride can be formed from methyl-compounds, ethylic

* H stands for the water-residue HO .

† Chem. Soc. J. [2] iv, 21.

chloride from ethylic hydride, and finally ethylic cyanide from ethylic chloride.

A mixture of acetic aldehyde, prussic acid and hydrochloric acid produces lactic acid—



The formation of malonic acid from acetic acid is another example of the same class.

On the other hand, by well known processes, we are able to resolve the propylic hydride group into derivatives of its proximate constituents.

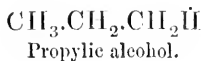
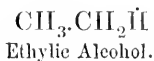
The formula $\text{CH}_3.\text{CH}_2.\text{CH}_3$ of propylic hydride enables us to predict* the existence of two isomeric alcohols $\text{C}_3\text{H}_8\text{O}$. If the

formula $\text{CH}_3.\text{CH}_2.\text{CH}_3$ be written thus, $b \begin{cases} a \text{ CH}_3 \\ \text{CH}_2 \\ c \text{ CH}_3 \end{cases}$ it is evident that

the same body will result whether 1 atom of hydrogen is replaced by $\ddot{\text{H}}$ in a or c . But a different body may be expected if the replacement takes place in b .

We obtain, therefore, $\begin{cases} \text{CH}_2\ddot{\text{H}} \\ \text{CH}_2 \\ \text{CH}_3 \end{cases}$ and $\begin{cases} \text{CH}_3 \\ \text{CH}\ddot{\text{H}} \\ \text{CH}_3 \end{cases}$, and two alcohols

of this composition are actually known. One, $\text{CH}_2\ddot{\text{H}}.\text{CH}_2.\text{CH}_3$ is obtained by fermentation†, the other, pseudo-propylic alcohol, may be prepared from different sources, viz., propylene‡, acetone§, acrolein||, allylic iodide¶, glycerin**, and propylglycol††. Both alcohols form ethers with acids, but they do not behave with oxidising agents in the same manner. One may be oxidised to propionic aldehyde and propionic acid, the other furnishes only acetone. The normal alcohol has evidently the same constitution as ethylic alcohol, and contains the water-residue in combination with CH_2 .



* The different hydrogen atoms in a hydrocarbon are supposed to possess the same chemical value.

† Anr. Ch. Pharm. lxxxvii, 127.

‡ Jahresbericht, 1855, 611; 1863 465.

§ Ann. Ch. und. Pharm. exxiv, 324; cxxxvi, 39.

|| Jahresbericht, 1863, 329.

¶ Ann. Ch. Pharm. cxxix, 128.

** Ann. Ch. Pharm. cxxvi, 309.

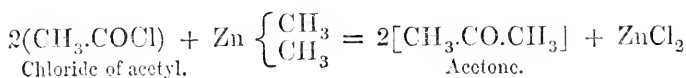
†† Jahresbericht, 1861, 655.

and accordingly it is able to produce propionic aldehyde $\text{CH}_3.\text{CH}_2.\text{COH}$ and acid $\text{CH}_3.\text{CH}_2.\text{COH}$. The pseudo-alcohol $\text{CH}_3.\text{CHH}.\text{CH}_3$ loses also under the influence of oxidising agents two atoms of hydrogen and is thus converted into acetone :



But acetone is not able, as is clear from this formula, to assimilate an atom of oxygen and produce an acid with the same number of carbon-atoms. Argentic oxide oxidises acetone at 100° to formic and acetic acids.

Chloride of acetyl and zinc methyl give, by double decomposition, zinc chloride and acetone :*



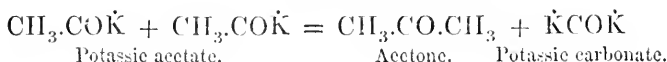
Nascent hydrogen and acetone combine to pseudo-propylic alcohol. The hydrogen can only attach itself to CO in $\text{CH}_3.\text{CO}.\text{CH}_3$, and therefore we obtain $\text{CH}_3.\text{CHH}.\text{CH}_3$ for pseudo-propylic alcohol. These two reactions confirm the formulæ of acetone and pseudo-propylic alcohol as deduced from the constitution of propylic hydride.

The alcohol obtained by Berthelot from propylene† is pseudo-propylic alcohol, whereas the body $\text{C}_2\text{H}_6\text{O}$ prepared by the same chemist from ethylene, is identical with ethylic alcohol formed during the fermentation of sugar. From ethylic hydride $\text{CH}_3.\text{CH}_3$, only one alcohol can be derived according to theory, for the result will be the same whether an atom of hydrogen is replaced by H in the first or second of the two groups CH_3 . The case is different with propylic hydride, as has been shown on page 259.

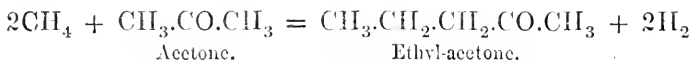
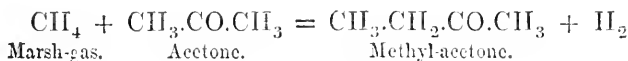
Acetone stands to pseudo-propylic alcohol in a relation similar to that which propionic aldehyde bears to propylic alcohol. The formation of this substance from zinc methyl and chloride of acetyl has already been mentioned, and according to this mode of preparation, it has the formula $\text{CH}_3.\text{CO}.\text{CH}_3$. The common source of acetone is, however, the destructive distillation of acetates.

* Ann. Ch. Pharm. cxviii, 11.

† Jahresbericht, 1855, p. 611.



Besides acetone, marsh-gas is liberated in consequence of a secondary reaction. If we conceive this marsh-gas at the moment of its liberation to act on acetone, the following bodies may result:—



bodies which are actually formed during the process, and have been liberated by Fittig from crude acetone. Both unite with bisulphite of soda and resemble acetone in their other chemical and physical properties.*

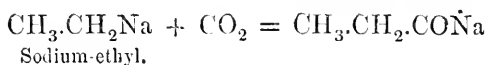
Acetone does not appear to be able to unite with acids;† at all events it does not do so with acetic acid; therefore the oxygen is not contained in it in the form H, as it is in ethylic alcohol. Oxidising agents convert acetone into acetic and formic acids, but do not produce an acid with 3 atoms of carbon in its molecule. Hence acetone cannot contain the group COH as a proximate constituent, because the latter is able to unite with an atom of oxygen and form COH. In fact, only the formula CH₃.CO.CH₃ is in accordance with the properties of acetone.

If two atoms of hydrogen are abstracted from propylic alcohol CH₃.CH₂.CH₂H, propionic aldehyde‡ CH₃.CH₂.COH remains which, in contact with air or argentic oxide, is converted into propionic acid CH₃.CH₂.COH. This formula is supported by the following reactions:—

a. Ethylic cyanide and caustic potash furnish propionate of potash and ammonia:



b. Sodium-ethyl and carbonic acid yield propionate of sodium:§



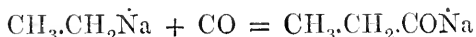
* Jahresbericht, 1859, p. 341.

‡ Ann. Ch. Pharm. cxxxiii, 182.

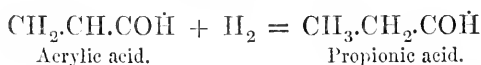
† Jahresbericht, 1863, 464.

§ Jahresbericht, 1860, 220.

c. Sodium-alcoholate and carbonic oxide from propionate of sodium :*



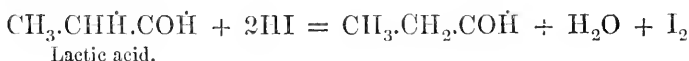
d. Sodium-amalgam converts acrylic acid into propionic acid :†



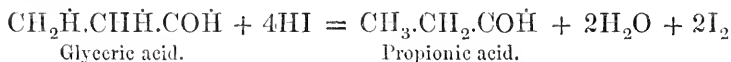
e. Pyruvic acid and HI form propionic acid, water, and iodine.‡



f. Hydriodic acid and lactic acid act at 100° on each other, and produce propionic acid, water, and iodine :§



g. Glyceric acid and hydriodic acid form at 200° propionic acid, water, and iodine :||



According to theory, only one acid of the composition of propionic acid ought to exist. The acid properties of organic compounds depend on the group COH, which is derived from CH₃.

Comparing the formulæ of propylic hydride and of propionic acid—



it is observed that the same body will be formed whether the group *a* or the group *c* in propylic hydride is converted into COH.

Lactic acid (α and β). According to the formula of propionic acid, two chlorine-, two bromine-, and two iodine-derivatives of this body, each containing one atom of the halogen, ought to exist. One atom of hydrogen may be replaced in *a* or *b* by chlorine $\text{CH}_3\text{CH}_2\text{CO}\dot{\text{H}}$, and thus we obtain two isomeric acids

* Jahresbericht, 1861, 108.

† Jahresbericht, 1863, 329.

‡ Ann. Ch. Pharm. exxvi, 229.

§ Jahresbericht, 1860, 274.

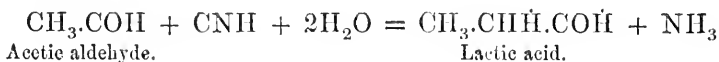
|| Jahresbericht, 1864, 370. Ann. Ch. Pharm. exx, 232.

$\text{CH}_2\text{Cl}.\text{CH}_2.\text{COH}$ and $\text{CH}_3.\text{CHCl}.\text{COH}$. If the chlorine is exchanged for the water-residue H , two acids, $\text{CH}_2\text{H}.\text{CH}_2.\text{COH}$ and $\text{CH}_3.\text{CHH}.\text{COH}$ of the composition of lactic acid would be formed. I adopt for ordinary lactic acid (β) the formula $\text{CH}_3.\text{CHH}.\text{COH}$, and for α -lactic acid, the acid of muscular tissue, the expression $\text{CH}_2\text{H}.\text{CH}_2.\text{COH}$. It will be shown further on that propyl-glycol must be represented thus:— $\text{CH}_3.\text{CHH}.\text{CH}_2\text{H}$. The oxidation of this substance* yields lactic acid just as common alcohol furnishes acetic acid. This process consists in the substitution of one atom of oxygen for two of hydrogen in the group CH_2H . Hence we have

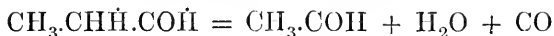
Ethylic alcohol	$\text{CH}_3.\text{CH}_2\text{H}$	Propyl-glycol	$\text{CH}_3.\text{CHH}.\text{CH}_2\text{H}$
Acetic acid	$\text{CH}_3.\text{COH}$	Lactic acid (β)	$\text{CH}_3.\text{CHH}.\text{COH}$

The following reactions confirm this view of the constitution of lactic acid:—

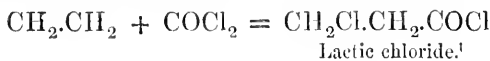
a. Acetic aldehyde, prussic acid, and hydrochloric acid form lactic acid:



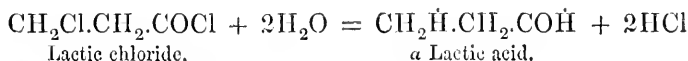
The hydrogen of the prussic acid enters the group COH of aldehyde, and converts it into CHH , the cyanogen exchanges with two atoms of water, nitrogen for OH , and then attaches itself to the altered aldehyde.† At a temperature above 140° lactic acid decomposes into water, aldehyde, and carbonic oxide:



b. Phosgene gas and ethylene form lactic chloride:



If the chlorine in this compound is replaced by H , α -lactic acid is obtained:‡

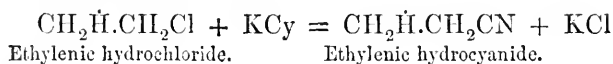


* Jahresbericht, 1858, 253.

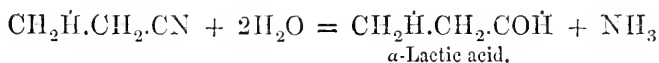
† Ann. Ch. Pharm. cxxviii, 22.

‡ Ann. Ch. Pharm. cxxix, 81.

c. From ethylenic hydrochloride, and cyanide of potassium principally α -lactic acid is formed :*



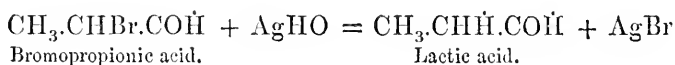
and if N in this cyanide is exchanged for OH, we obtain α -lactic acid :



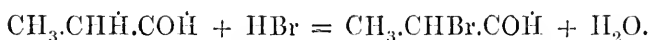
α -lactic acid may, however, be converted into β -lactic acid, so that it appears that the latter is the more stable compound. This change is effected by heating $\text{CH}_2\dot{\text{H}}.\text{CH}_2.\text{CO}\dot{\text{H}}$ to 140° until it is converted into anhydrous lactic acid, and the latter, on boiling it with water, forms a solution of β -lactic acid $\text{CH}_3.\text{CH}\dot{\text{H}}.\text{CO}\dot{\text{H}}.$ †

Other interesting formations of lactic acid are the following :—

d. Bromopropionic acid treated with argentic oxide forms lactic acid and argentic bromide :‡

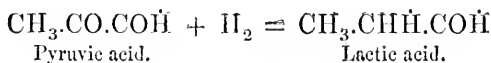


Conversely, by heating lactic acid with hydrobromic acid, bromopropionic acid and water are obtained :



Sodium-amalgam converts bromopropionic acid into propionic acid.§

e. Pyruvic acid and nascent hydrogen (from Zn and acetic acid) produce lactic acid :||



f. Iodoform and sodium-alcoholate form an ether of lactic acid :¶

* Ann. Ch. Pharm. cxxviii, 2.

† Jahresbericht, 1858, 254.

‡ Ann. Ch. Pharm. cxx, 285.

§ Ann. Ch. Pharm. cxxx, 11.

|| Ann. Ch. Pharm. cxxvi, 227 ; cxxvii, 532.

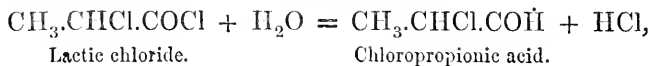
¶ Jahresbericht, 1861, 379.

disodic compound. The latter, however, decomposes immediately in contact with water into sodic hydrate and ordinary lactate. Lactic acid is, therefore, said to possess the properties of an acid and an alcohol (Perkin, Wurtz, Friedel, Wislicenus.)* This behaviour of lactic acid is owing to the different constitution of groups *b* and *c*.† To the same cause must be referred the difference which exists in the behaviour of alanine‡ and lactamide. The former is represented by $\text{CH}_3.\text{CH}(\text{NH}_2).\text{COH}$ and the latter by $\text{CH}_3.\text{CHH}.\text{CO}(\text{NH}_2)$. Alanine, therefore, still comports itself like an acid.

We are acquainted with two isomeric ethers of lactic acid—one is an acid and the other a neutral compound.§ Representing the first by the formula $\text{CH}_3.\text{CHEt}.\text{COH}$, we understand why this substance still possesses the properties of an acid and is not decomposed by a solution of caustic potash into alcohol and an ordinary lactate, because the group ethyl occupies in the compound a position similar to that which it has as in ethylic ether $\left. \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{O}$, and the latter also is not transformed by potassic hydrate into two atoms of alcohol. The body discovered by Strecker is neutral and decomposed by water into lactic acid and alcohol; its constitution may be represented thus:—

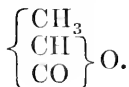


Further, the two chlorine-atoms in lactic chloride do not comport themselves in exactly the same manner. Water easily exchanges one atom of chlorine for the residue H :



producing chloropropionic and hydrochloric acids. The second atom of chlorine can, however, be exchanged in the same manner by treating $\text{CH}_3.\text{CHCl}.\text{COH}$ with potassic hydrate at 100° ; the result being potassic lactate, water, and potassic chloride.

Lactide or anhydrous lactic acid is represented by the formula



* Chemical News, 1861, 81; Ann. Ch. Pharm. cxix, 369; cxxv, 52.

† Chem. Soc. Journ. [2] iv, 24, 26.

‡ Jahresbericht, 1860, 275.

§ Jahresbericht, 1852, 495; and 1860, 272.

Pyroracemic or *Pyruvic acid* $C_3H_4O_3$. The properties of this body have not been sufficiently investigated to allow us to fix its rational formula with a great degree of probability. Two modifications are known—one boils at 165° , and forms with bases crystallisable salts, the other is gummy, and produces amorphous compounds with metallic oxides.* The formula $CH_3.CO.CO\dot{H}$ seems to agree best with our present knowledge. According to this view of its constitution it stands to lactic acid in the same relation as acetone does to pseudo-propylic alcohol :

Lactic acid.....	$CH_3.CH\dot{H}.CO\dot{H}$
Pyruvic acid.....	$CH_3.CO.CO\dot{H}$
Pseudopropylic alcohol.....	$CH_3.CH\dot{H}.CH_3$
Acetone.....	$CH_3.CO.CH_3$

Nascent hydrogen, prepared by means of sodium amalgam, changes acetone to pseudo-propylic alcohol, and pyruvic acid into lactic acid.† There is also much resemblance between pyruvic acid and acetone in their respective comportment with bromine and basic oxides. α -lactic acid will, in all probability, lose, in contact with bromine, two atoms of hydrogen, and produce an acid of the same composition as pyruvic acid, but endowed with different properties. This acid, $CO\dot{H}.CH_2.CO\dot{H}$, would be homologous to glyoxylic acid, possess the properties of an acid and an aldehyde, and be converted by dilute nitric acid into malonic acid. Pyroracemic acid does not possess such properties. I have made two or three experiments with the intention of converting it into malonic acid, but without the desired result. Pyruvic acid is acted on by a mixture of nitric acid, water, and platinum-black, at temperatures not exceeding 20° or 30° , but the principal product of the oxidation is glycollic acid.

Malonic acid, $C_3H_4O_4$, as a bibasic acid, must contain the group $CO\dot{H}$ twice, and accordingly we have for its rational formula $CO\dot{H}.CH_2.CO\dot{H}$, an expression which is confirmed by H. Müller's and Kolbe's elegant reaction.‡ If in acetic acid an atom of hydrogen be replaced by cyanogen, we have



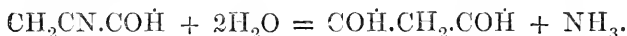
This cyanogen derivative of acetic acid decomposes with potassic

* Ann. Ch. Pharm. lxxxix, 65.

† Ann. Ch. Pharm. cxxvi, 225; cxxvii, 332.

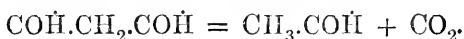
‡ Chem. Soc. J. [2], ii, 109; Ann. Ch. Pharm. cxxxi, 348, 350.

hydrate in the well known manner, N being exchanged for OH of two atoms of water yielding malonic acid and ammonia.

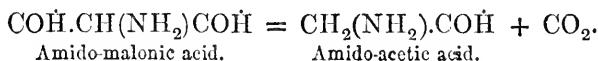


Malonic acid therefore contains the three groups $\text{COH}.\text{CH}_2.\text{COH}$. It may also be prepared from barbituric acid, a derivative of alloxan,* and by oxidizing malic acid by means of chromate of potash.†

It is easy to reproduce acetic acid from malonic acid. For this purpose it is sufficient to heat the latter to 150° , when it decomposes according to the following equation :



In a similar manner amido-malonic acid is transformed into amido-acetic acid and carbonic acid.‡

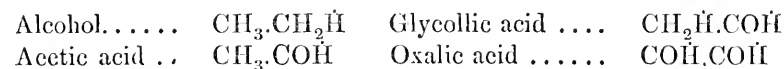


Both decompositions, taken in connection with the formation of malonic acid from a derivative of acetic acid, are greatly in favour of the constitution of malonic acid, expressed in the formula $\text{COH}.\text{CH}_2.\text{COH}$.

As oxalic acid is easily obtained by the oxidation of glycollic acid, the formation of malonic acid from lactic acid [β] by a similar process might be expected.

The formula given for lactic acid [β] in this paper shows that such cannot be the case. The oxidation, as a rule, commences in that group in which the water-residue H is contained.

The relation of acetic acid to alcohol, and that of oxalic to glycollic acid, is represented by the following formulæ:



A transformation of this nature cannot take place with lactic acid, $\text{CH}_3.\text{CH}.\text{COH}$, because the group CHH cannot be changed into COH . Lactic acid [β] will, however, in all probability be oxi-

* Ann. Ch. Pharm. cxxx, 143.

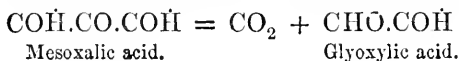
† Ann. Ch. Pharm. cvii, 251 ; Compt. rend. xlvii, 76.

‡ Jahresbericht, 1864, 639.

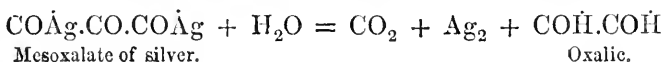
dised to pyruvic acid, $\text{CH}_3\text{CO.CO}\dot{\text{H}}$, just as pseudo-propylic alcohol is converted by bromine into acetone. Malonic acid ought to be formed by the oxidation of α -lactic acid.

Tartronic acid, $\text{C}_3\text{H}_4\text{O}_5$,* first observed by Dessaignes as a product of the spontaneous decomposition of nitro-tartaric acid, is a bibasic acid, and has the formula $\text{CO}\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{CO}\dot{\text{H}}$.

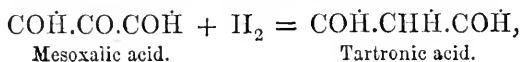
Mesoxalic acid, $\text{C}_3\text{H}_2\text{O}_5$, stands to tartronic acid in the same relation as pyruvic acid does to lactic acid, or acetone to pseudo-propylic alcohol. It is easily decomposed, even in its aqueous solution at 70° or 80° , into unknown products. According to analogy, carbonic and glyoxylic acids ought to be formed.



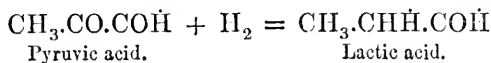
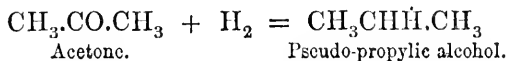
With this conclusion agrees the decomposition of the silver-salt at 100° into metallic silver, carbonic acid, and oxalic acid.



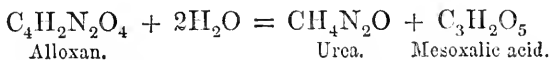
Sodium-amalgam converts mesoxalic acid into tartronic acid;



just as acetone is transformed into pseudo-propylic alcohol or pyruvic acid into lactic acid.



Alloxan yields mesoxalic acid according to the following equation:†—

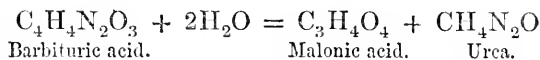


One atom of oxygen in alloxan may be replaced by H_2 . The new body thus obtained has been called *barbituric acid*, and may be decomposed by means of potassic hydrate into malonic acid and urea, or, instead of urea, carbonic acid and ammonia.‡

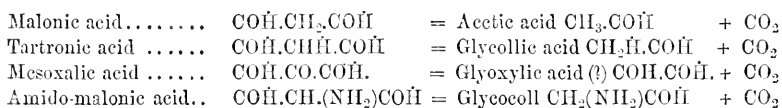
* Ann. Ch. Pharm. lxxxii, 362; lxxix, 339.

† Jahresbericht, 1864, 642.

‡ Jahresbericht, 1864, 634.



These decompositions, and the formula $\text{C}_3(\text{NH}_4)_2\text{O}_5$ of the ammonia-salt, determine the composition of mesoxalic acid. We are thus able to ascend directly from mesoxalic acid to tartronic, and indirectly to malonic acid. It is interesting to consider for a moment the decomposition of these acids under the influence of heat.



The process consists, then, in the transfer of an atom of H from the group COH to the next carbon group, and the escape of the residue thus left as carbonic acid.

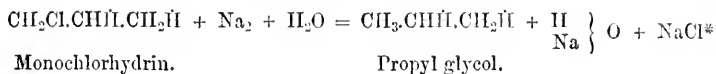
If two atoms of hydrogen be abstracted from propylic hydride, the hydrocarbon C_3H_6 , propylene, is left. One atom of hydrogen is taken from the group CH_2 , and the other from one of the groups CH_3 . Thus we obtain for propylene the formula $\text{CH}_3\text{.CH.CH}_2$. Accordingly, propylene can again unite with two chemical units, and produce a derivative of propylic hydride. If bromine be chosen for this purpose, propylenic bromide $\text{CH}_3\text{.CHBr.CH}_2\text{Br}$ is formed. This compound may, by a well known method, be converted into

Propyl-glycol, $\text{C}_3\text{H}_8\text{O}_2^* = \text{CH}_3\text{.CHH.CH}_2\text{H}$. Two other interesting modes of forming this body deserve to be mentioned. Acetone combines with nascent hydrogen, and produces pseudo-propylic alcohol, $\text{CH}_3\text{.CHH.CH}_3$, which readily exchanges the water-residue H for iodine with hydriodic acid. Bromine displaces the iodine in pseudo-propylic iodide, $\text{CH}_3\text{.CHH.CH}_3$, and originates the corresponding bromide, $\text{CH}_3\text{.CHBr.CH}_3$. If another molecule of bromine is made to act on the latter, hydrobromic acid and propylenic bromide are obtained.† From propylenic bromide, by means of Wurtz's method, propyl-glycol can be prepared. This series of reactions leads to the formula $\text{CH}_3\text{.CHBr.CH}_2\text{Br}$ for propylenic bromide, and confirms thereby the above formula for propyl-glycol.

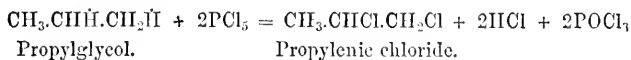
Mono-chlorhydrin, sodium-amalgam, and water form propyl-glycol, chloride of sodium, and sodic hydrate—

* Ann. Ch. Pharm. cv, 262.

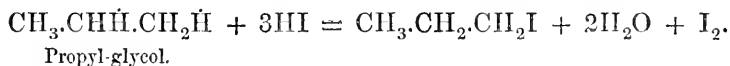
† Ann. Ch. Pharm. cxxvi, 54.



Pentachloride of phosphorus acts on propyl-glycol and replaces the water-residues by chlorine.

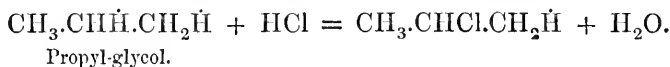


Hydriodic acid converts propyl-glycol into propylic iodide.†

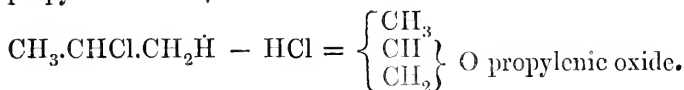


Whether this iodide is propylic or pseudo-propylic iodide has not, so far as I am aware, been determined.

Hydrochloric acid acts on propyl-glycol in the same manner as on ethyl-glycol. One of the groups, $\dot{\text{H}}$, is replaced by chlorine—

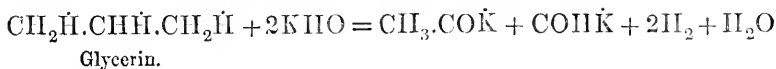


Solution of caustic potash abstracts from the chloride $\text{CH}_3.\text{CHCl}.\text{CH}_2\dot{\text{H}}$, a molecule of hydrochloric acid, and forms propylenic oxide.‡



Glycerin is a triatomic alcohol, and for reasons given in the first part of this paper§ I represent it by the formula $\text{CH}_2\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{CH}_2\dot{\text{H}}$. The hydrogen of the water residues may be replaced by one, two, or three acid or basic radicals, or one, two, or the three groups $\dot{\text{H}}$ by chlorine or bromine.||

1. One of the three groups which we assume to exist in glycerin may be separated from the other two by the action of potassic hydrate at a high temperature. Oxidation takes place, potassic acetate and formate being produced :



* Jahresbericht, 1861, 655; Ann. Ch. Pharm. cxx, 89.

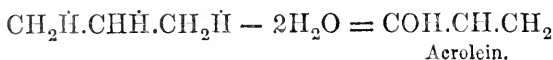
† Jahresbericht, 1861, 655.

§ Chem. Soc. J. [2], iv, 26.

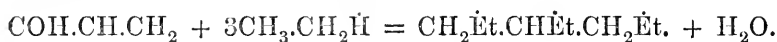
‡ Jahresbericht, 1860, 443.

|| Chem. Soc. Qu. J. xii, 242.

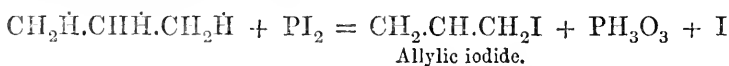
2. Glycerin heated with anhydrous phosphoric acid loses two atoms of water, and yields acrolein :



Acrolein combines directly with alcohols and forms ethers of glycerin :*

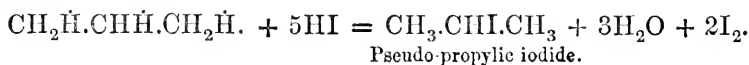


3. Iodide of phosphorus and glycerin produce allylic iodide, phosphorus acid, and iodine :†

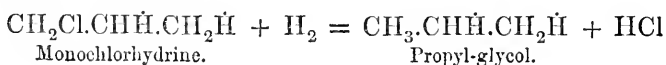


In this case the three water-residues are abstracted and replaced by one atom of iodine ; a derivative of propylic hydride is converted into one of propylene.

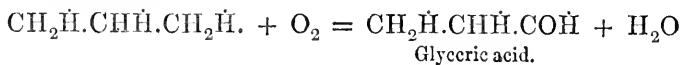
4. Hydriodic acid and glycerin form water, iodine, and pseudo-propylic iodide :‡



5. Monochlorhydrin and sodium-amalgam yield propyl-glycol :§



6. Nitric acid replaces in glycerin two atoms of hydrogen by one of oxygen :||



Glyceric acid is a monobasic acid because the group COH occurs only once in it. The replacement of the hydrogen of the water-residues in CH₂H and CHH by negative or chlorous radicals, may, however, be expected.

* Jahresbericht, 1864, 494.

† Jahresbericht, 1854, 451 ; Ann. Ch. Pharm. xcii, 306.

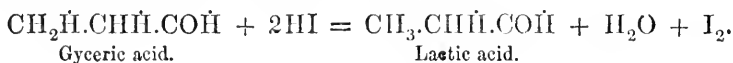
‡ Ann. Chem. Pharm. cxxvi, 305 ; Supp. iii, 267.

§ Ann. Ch. Pharm. cxx, 89.

|| Phil. Mag. March, 1858 ; Ann. Ch. Pharm. cvi, 81.

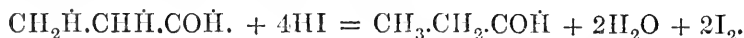
The three groups H in glyceric acid may, like those in glycerin, be removed or replaced by equivalent groups or atoms of another character. The introduction of two atoms of H for two H produces propionic acid; the substitution of one of H for one of H produces lactic acid; the replacement of one H by I and of another H by chlorine or iodine, furnishes chloropropionic and iodopropionic acids respectively. These transformations take place under the influence of the following reagents:—

a. An aqueous solution of hydriodic acid and glyceric acid produce at 200° lactic acid, water, and iodine:



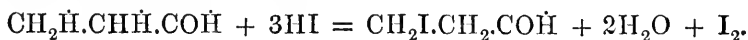
The same result is obtained when glycerates are heated with potassic hydrate.*

Under the conditions just named, hydriodic converts a portion of glyceric acid into propionic acid:†

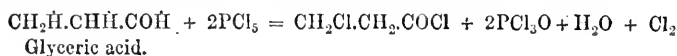


These reactions correspond to the formation of propyl-glycol and pseudo-propylic alcohol from glycerin.

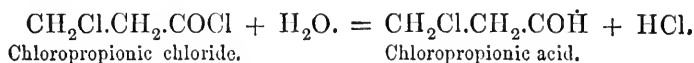
b. If, however, glyceric acid be treated with a concentrated solution of hydriodic acid at 100° , two water-residues are also removed, but one is replaced by H and the other by I . The product is iodopropionic acid:‡



c. Pentachloride of phosphorus and glyceric acid react on each other as represented by the following equation:—



$\text{CH}_2\text{Cl}.\text{CH}_2.\text{COCl}$ in contact with water forms chloropropionic and hydrochloric acids:



How the chlorine, which is liberated according to the above equa-

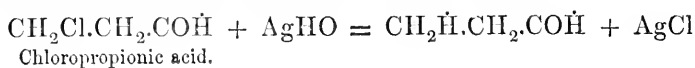
* Phil. Mag. Dec. 1858; Ann. Ch. Pharm. cix, 227.

† Ann. Ch. Pharm. cxxxi, 223, 326.

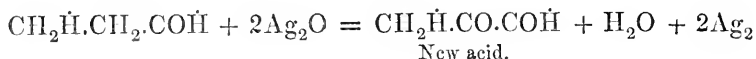
‡ Ibid.

tion, is disposed of is not known. This reaction is very interesting, because generally pentachloride of phosphorus substitutes chlorine for the water residue $\dot{\text{H}}$ in organic acids. It is, however, analogous to that between glyceric acid and iodide of phosphorus. Whether this chloropropionic acid is identical or isomeric with the one obtained from lactic acid remains to be determined.

The iodopropionic and chloropropionic acids prepared from glyceric acid decompose by boiling with argentic oxide, with formation of argentic iodide and chloride, respectively, and separation of metallic silver. In the case of iodopropionic acid argentic lactate originates, but the nature of the products of oxidation has not been ascertained. Whether the chloropropionic acid yields, under the same conditions, argentic lactate, remains to be seen, but it is known that it furnishes the silver-salt of an acid, the analysis of which agrees with the formula $\text{C}_3\text{H}_4\text{O}_4$:

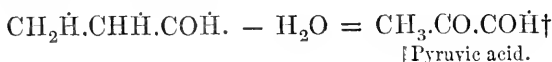


and



The chemical properties of this interesting acid ($\text{CH}_2\dot{\text{H}}.\text{CO}.\text{CO}\dot{\text{H}}$) require investigation.*

If glyceric acid be subjected to destructive distillation, pyruvic acid and water are obtained.



Propylene and its derivatives.

The formula of this hydrocarbon is $\text{CH}_3.\text{CH}.\text{CH}_2$. Some of the derivatives of propylic hydride exhibit the tendency to lose, under certain conditions, two chemical units, and to become converted into propylene itself, or in bodies which may be considered as derivatives of the same. Iodide of phosphorus and glycerin produce allylic iodide and propylene. The iodide of allyl can, as the important researches of Cahours and Hofmann have shown, be converted by double decomposition into allylic alcohol, and from the latter, by processes of oxidation, acrolein and acrylic

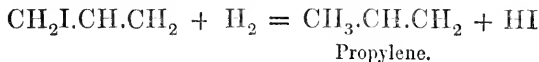
* Ann. Ch. Pharm. cxxxi, 329; cxxxv, 251, 255, 256.

† Ann. Ch. Pharm. cxxxi, 337.

acid may easily be prepared. Now, allylic iodide, in order to allow of its transformation into allylic alcohol and acrylic acid, must contain the group CH_2I , therefore the three remaining hydrogen-atoms of allylic iodide divide themselves between the other two carbon-atoms and the formula of allylic iodide, must be $\text{CH}_2\text{I}.\text{CH}.\text{CH}_2$. Replacing in this the iodine by means of well-known reactions, by the water residue H , we obtain allylic alcohol $\text{CH}_2\text{H}.\text{CH}.\text{CH}_2$, from the latter by oxidation, acrolein $\text{COH}.\text{CH}.\text{CH}_2$ and acrylic acid $\text{COH}.\text{CH}.\text{CH}_2$. All these transformations are analogous to those of ethylic iodide into ethylic alcohol, aldehyde and acetic acid :

Ethylic iodide ..	$\text{CH}_3.\text{CH}_2\text{I}$	Allylic iodide, ..	$\text{CH}_2\text{I}.\text{CH}.\text{CH}_2$
Ethylic alcohol ..	$\text{CH}_3.\text{CH}_2\text{H}$	Allylic alcohol.	$\text{CH}_2\text{H}.\text{CH}.\text{CH}_2$
Acetic aldehyde.	$\text{CH}_3.\text{COH}$	Acrolein	$\text{COH}.\text{CH}.\text{CH}_2$
Acetic acid	$\text{CH}_3.\text{COH}$	Acrylic acid ..	$\text{COH}.\text{CH}.\text{CH}_2$

By means of hydrochloric acid and mercury, allylic iodide may be converted into propylene, that is to say, the iodine is simply replaced by hydrogen.* Therefore we obtain :

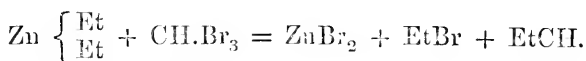


If the formula of propylene be compared with that of propylic hydride, it is perceived that two of the residues of the latter, which are attached to each other, lose each an atom of hydrogen, and thus from the molecule propylic hydride results the stable molecule propylene :



The formula of propylene thus deduced from allylic iodide contains three different marsh-gas residues $\text{CH}_3.\text{CH}.\text{CH}_2$. To this circumstance must be mainly attributed the manifold properties which this body exhibits, when regarded from different points of view.

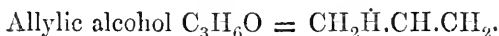
The formation of propylene from bromoform and zinc-ethyl† confirms the formula $\text{CH}_3.\text{CH}.\text{CH}_2$:



* Jahresbericht, 1854, 453.

† Jahresbericht, 1864, 470.

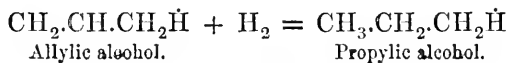
Now, ethyl* itself is composed of the residues $\text{CH}_3\cdot\text{CH}_2\cdot$, and therefore according to this simple reaction, we have the same three groups $\text{CH}_3\cdot\text{CH}_2\cdot$ and $\text{CH}\cdot$ in propylene, which had been recognised as the proximate constituents of this body by reasoning from quite a different basis.



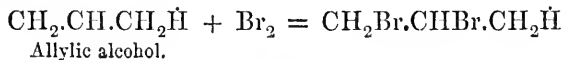
We may conceive this alcohol as propylic alcohol, minus two atoms of hydrogen. If one of the marsh-gas residues in propylic alcohol loses an atom of hydrogen, it is clear that the equilibrium of the molecule must thereby be destroyed. If, however, another of the residues, which is in direct union with the former, also loses an atom of hydrogen, a new and stable molecule may result :†



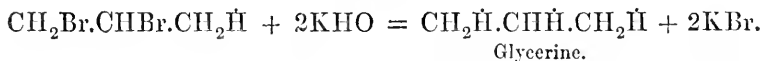
But the two units may be taken up again by allylic alcohol, and by changing in successive experiments the quality of these units, a whole host of derivatives may be prepared. Allylic alcohol possesses then the double character of an alcohol and of a biatomic radical. Sodium-amalgam, in contact with water, adds to allylic alcohol two atoms of hydrogen, and the normal propylic alcohol ought to result :



Bromine combines directly with allylic alcohol and produces a bromide from which, by replacement of the bromine by the water residue $\dot{\text{H}}$, glycerin may be obtained :‡



and



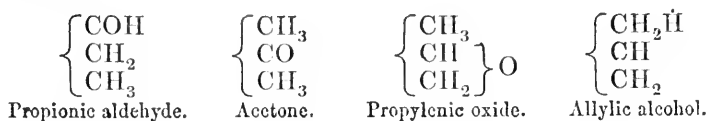
The alcoholic properties of allylic alcohol are well known, and therefore need no illustration.

* Chem. Soc. J. [2], iv, 22.

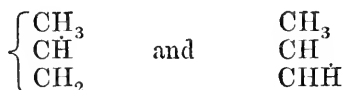
† Ibid., 21 and 25.

‡ Jahresbericht, 1864, 490; Kekulé, *Lehrbuch* II. 263, 264.

In order to show how the four isomeric bodies of the empirical formula C_3H_6O differ in constitution, their rational formulæ are subjoined :



Oxygen may be contained in a body composed of carbon hydrogen and oxygen, as a substitute for hydrogen in the place of two atoms of this element, or in near relation to hydrogen, as the water residue H. The above list shows that, as far as the first mode of existence of oxygen in bodies of the formula C_3H_6O is concerned, the list of isomeric bodies with three atoms of carbon, six of hydrogen, and one of oxygen, is complete,* whereas two more bodies are wanting with their oxygen contained in the group H :



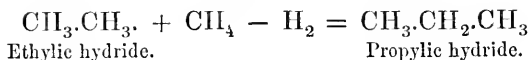
thus making three isomeric bodies of each class, altogether, from a theoretical point of view, six substances of the empirical formula C_3H_6O .

The group C_3H_5 occurs in some compounds as a monatomic and in others as a triatomic radical. As the cause of this peculiarity is not generally understood, I will introduce the explanation of it in this place.

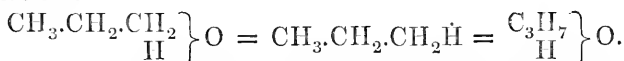
Propylic hydride is composed of three marsh-gas residues. Whatever the cause may be that keeps the atoms in a molecule united, there can be no doubt that when an atom of hydrogen is abstracted from a complete molecule, the effect of such removal must be a certain resultant force, and the equilibrium between the atoms of the molecule is destroyed. If the same alteration is effected in another molecule, a resultant of the same magnitude must originate.

If the two incomplete molecules are placed together in such a manner that the two equal resultants can counteract each other, a new, more complex, and stable molecule is obtained. We may conceive in this way the production of propylic hydride from ethylic hydride and marsh-gas.

* If all the hydrogen-atoms possess the same chemical value.

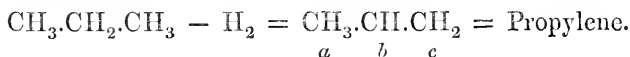


If, now, by indirect means, an atom of hydrogen is abstracted from $\text{CH}_3.\text{CH}_2.\text{CH}_3$, and an atom of hydrogen from a molecule of water, the two incomplete molecules may remain in chemical combination :



To say that the hydrocarbon-radical, C_3H_7 replaces an atom of hydrogen in water is in a certain sense correct, but does not express the whole relation. It is just as legitimate to say that the water residue $\dot{\text{H}}$ replaces an atom of hydrogen in C_3H_7 . One or the other mode of representation may have advantages in particular cases, and may be preferred to the other. The mechanical conception given embraces both considerations.

What takes place between two distinct molecules, water and propylic hydride, may also occur between the proximate constituents of the same molecule. If each of two residues in propylic hydride loses an atom of hydrogen, the stable molecule propylene will be the result—



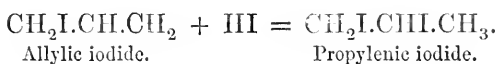
The molecule of the latter plays a double function ; if an atom of hydrogen be replaced in group *a* by iodine, we obtain a body which comports itself like an iodide of an alcohol-radical, but it can also combine again with two chemical units (groups *b* and *c*), and thus act like a biatomic radical.

By replacement of the iodine by simple or compound radicals, we can prepare from allylic iodide $\text{CH}_2\text{I}.\text{CH}.\text{CH}_2$, a class of bodies similar to those produced from ethylic iodide. It is the group *a* only that is affected by the reactions. If, however, bromine is made to act on allylic iodide, the groups *b* and *c* unite again with two units in the form of bromine, and finally the iodine is replaced by bromine and the so-called allylic tribromide $\underset{a}{\text{CH}_2}\text{Br}.\underset{b}{\text{CH}}\text{Br}.\underset{c}{\text{CH}_2}\text{Br}$ is produced. From this body glycerin can

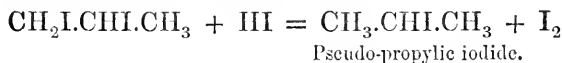
be formed by the exchange of the bromine for the water-residue H . The formula of glycerin, $\text{CH}_2\text{H}.\text{CHH}.\text{CH}_2\text{H}$, may be written thus : $\left. \text{C}_3\text{H}_5 \right\} \text{O}_3$, and accordingly we consider the group

C_3H_5 to play the part of a triatomic radical. Therefore, whether C_3H_5 is triatomic or monatomic depends upon whether we start with the bromide $CH_2Br.CHBr.CH_2Br$, or with $CH_2Br.CH.CH_2$. In the former case all three marsh-gas residues are brought into action; in the latter case only one. Which of the two takes place depends on the conditions of the experiment.

The action of hydriodic acid on allylic iodide is explained in the same manner.* In the first stage it combines with hydriodic acid.

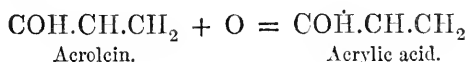
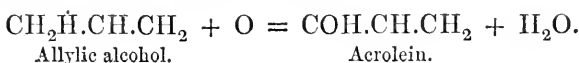


Propylenic iodide is decomposed by HI in the second stage of the reaction in the following manner:—

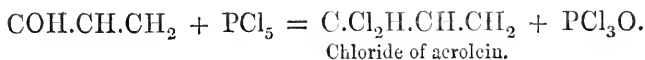


In this manner we pass from a derivative of propylene to one of propylic hydride. All allylic compounds ought to comport themselves as biatomic radicals.

Acrolein and Acrylic Acid are produced in succession when oxidising agents act on allylic alcohol:



Acrolein in its chemical properties resembles acetic aldehyde. Like the latter, it absorbs oxygen in contact with air, and exchanges with pentachloride of phosphorus an atom of O for two of chlorine.†



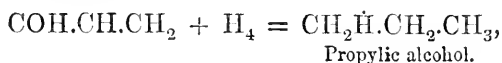
The chloride of ethylidene (prepared from acetic aldehyde) loses, in contact with an alcoholic potash-solution, the elements of hydrochloric acid, and forms vinylic chloride, C_2H_3Cl . The chloride from acrolein undergoes a similar decomposition with the

* Ann. Ch. Pharm. cxxix, 128.

† Jahresbericht, 1860, 305; *ibid.* 1864, 334. *Zeitschrift für Chemie*, 1865, 29.

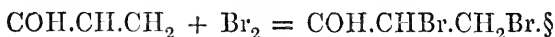
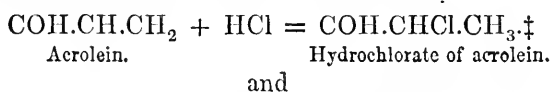
same reagent, the new chloride, C_3H_3Cl , being produced.* These properties establish the close relationship between acetic aldehyde and acrolein. However, like allylic alcohol and iodide, it is able to combine directly with hydrogen, or with chlorine, bromine, hydrochloric and hydriodic acids respectively.

Hydrogen may be introduced into the acrolein molecule by means of sodium amalgam : †



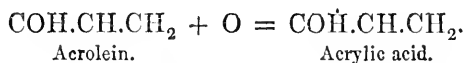
and convert the same into propylic alcohol. Allylic alcohol being intermediate between acrolein and propylic alcohol, would, no doubt, be produced if the reaction could be arrested after the addition of two atoms of hydrogen to acrolein.

The following combinations appear to have been effected :—

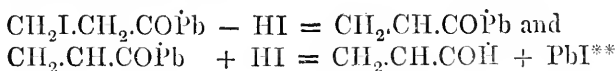


On account of the relation of acrolein to allylic alcohol, on the one hand, and to acrylic acid on the other hand ; and with regard to its analogy to acetic aldehyde, we assume in it the group $COH\|$, and in order to explain its ability to combine with bromine or hydrogen, the two groups CH and CH_2 . The formula $COH.CH.CH_2$ is, therefore, the representation of this double character of acrolein.

The formation of acrylic acid from acrolein has already been mentioned :



This acid is also formed when iodopropionate of lead is exposed to a high temperature : ¶



* Jahresbericht, 1864, 332, 333.

‡ Kekulé, *Lehrbuch* ii, 2717.

§ Chem. Soc. J. [2], iv, 23, 24.

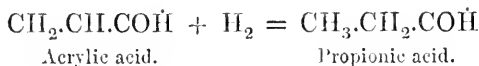
† Ann. Ch. Pharm. cxxv, 315.

§ Jahresbericht, 1864, 332.

¶ Ann. Ch. Pharm. cxxii, 372.

** In order to simplify the formula, $Pb = 103.4$.

The two units which iodopropionic acid has lost in this reaction may be united again with acrylic acid. Sodium-amalgam and acrylic acid yield propionic acid.*



It appears also that acrylic acid and bromine are able to form a compound.†

Acrylic acid and the acids homologous with it, break up in contact with potassic hydrate at a higher temperature into two new acids, of which one is always acetic acid. If the formulæ of propionic and acrylic acids, $\text{CH}_3.\text{CH}_2.\text{COH}$ and $\text{CH}_2.\text{CH}.\text{COH}$, be compared with each other, it is seen that the two residues CH and CH_2 in acrylic acid are more intimately connected, and accordingly held together by a more intense force than they are with the third residue, COH . This is owing to the fact that the marsh-gas molecules from which CH and CH_2 are derived have lost more chemical units than the marsh-gas to which the group COH is related. Two groups of this nature must occur in all compounds homologous with acrylic acid, and this circumstance, perhaps, explains the fact that always in this class of bodies two of the groups separate in the form of acetic acid.

I conclude the oxygen derivatives of propylic hydride and propylene with two new bodies recently obtained by Carius,‡ although both substances are little known, and require further investigation. These two compounds are propyl-phycite and an acid obtained by its oxidation. Carius expresses the composition of the first by the formula $\left. \begin{array}{c} \text{C}_3\text{H}_4 \\ \text{H}_4 \end{array} \right\} \text{O}_4$, and calls it an alcohol.

Propyl-phycite is an amorphous, viscous mass, which decomposes with the greatest facility. If its aqueous solution is evaporated with a few per cent. of acetic acid, brown products of the appearance of humus are formed. Only one atom of hydrogen could be replaced in propyl-phycite by the radical NO_2 , two by the radical $\text{C}_2\text{H}_3\text{O}$, and two by lead. The nitric and acetic acid derivatives are amorphous, like the mother-substance from which they had been prepared. The lead compound appeared under the microscope indistinctly crystalline. Other compound:

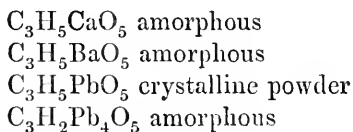
* Jahresbericht, 1863, 329.

† Ann. Ch. Pharm. Supp. ii, 33.

‡ Ann. Ch. Pharm. cxxxiv, 71.

are not known. The formula $\left. \begin{smallmatrix} \text{C}_3\text{H}_4 \\ \text{H}_4 \end{smallmatrix} \right\} \text{O}_4$, is, therefore, hypothetical.

The acid obtained by the oxidation of propyl-phycite is also amorphous, and has not been analysed. The following salts have been formed with it :—

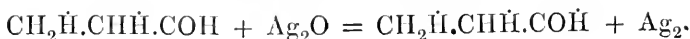


The acid has not been investigated in other respects, and, therefore, its formula, like that of propyl-phycite, must be determined by further researches.

I believe the formula $\text{CH}_2\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{COH}$ for propyl-phycite, and $\text{CH}_2\dot{\text{H}}.\text{CO}.\text{CO}\dot{\text{H}}$ for the acid obtained by its oxidation by means of nitric acid, are better supported by the evidence at present in our possession than the formulæ of Carius.* Propyl-phycite resembles the members of the sugar group very closely. It dissolves lime and baryta, the oxides of lead and silver, is easily decomposed by acids into brown masses, having the appearance of humus, and has a very sweet taste. Now, no member of the sugar group contains more oxygen atoms than carbon-atoms, and of all other alcohols the same may be said. This, together with the fact that no compound of propyl-phycite with four hydrogen-atoms replaced by a negative radical is known, although Carius tried to produce such, induces me to assume that the substances investigated by Carius were hydrates, that the formula of propyl-phycite is $\text{C}_3\text{H}_6\text{O}_3$, and of the acid $\text{C}_3\text{H}_4\text{O}_4$, instead of $\text{C}_3\text{H}_8\text{O}_4$ and $\text{C}_3\text{H}_6\text{O}_5$ respectively.

The rational formulæ $\text{CH}_2\dot{\text{H}}.\text{CH}\dot{\text{H}}.\text{COH} = \text{C}_3\text{H}_6\text{O}_3$ is supported by the chemical properties of propyl-phycite. It explains why only two atoms of hydrogen can be replaced in this substance by metals or acid radicals, and accounts for the changeable nature of the same by the presence of the aldehyde-group COH . Argentic oxide is, with the greatest ease, reduced to metallic silver by propyl-phycite, and when it is employed in the preparation of propyl-phycite, this body is not obtained, but in its place a substance of the empirical formula $\text{C}_3\text{H}_6\text{O}_4$.

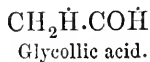
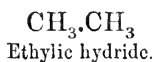
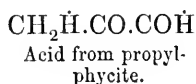
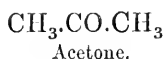
* Chem. Soc. J. [2] iv, 26 and 27.



The properties of this product of oxidation have, apparently, not been investigated, and, therefore, it is uncertain whether it is identical with glyceric acid or not.

Glyoxal, $\text{COH}.\text{COH}$, possesses the properties of an aldehyde, and stands to glycol in a relation similar to that which acetic aldehyde bears to ethylic alcohol. According to the formula $\text{CH}_2\text{H}.\text{CHH}.\text{COH}$ propyl-phycite is the first aldehyde of glycerin.

The acid formed by the action of nitric acid on propyl-phycite has the same relation to acetone as glycollic acid to ethylic hydride—



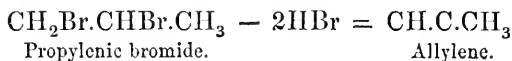
and is perhaps identical with that obtained by the decomposition of chloropropionic acid by means of argentic oxide.

Allylene contains two atoms of hydrogen less than propylene, and is formed by the action of potash-solution on propylenic bromide and bromo-propylene $\text{C}_3\text{H}_5\text{Br}$, respectively, or by the removal of chlorine from the chloride of dichloracetone or the chloride of epidichlorhydrin.*

Acetylene contains the two groups $\text{CH}.\text{CH}$, and at least one atom of hydrogen in this arrangement is distinguished by its aptitude to give way to metals. This property we meet again in allylene, and, therefore, assume that it contains, like acetylene, the group CH . The three remaining atoms of hydrogen must be joined to one atom of carbon, and accordingly we obtain for allylene

the formula $\text{CH}.\text{C}.\text{CH}_3$ or $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{C} \\ \text{CH} \end{array} \right.$. The conversion of propylenic

bromide into allylene consists, therefore, in the removal of the elements hydrogen and bromine from the groups CHBr and CH_2Br .



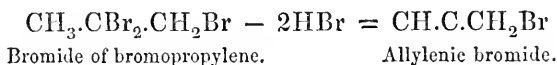
Allylene passed through a solution of argentic nitrate and

* Ann. Ch. Pharm. Jan. 1865, 121; September, 1865, 368, 371.

ammonia yields a precipitate $C_3H_3Ag = \begin{Bmatrix} CH_3 \\ C \\ CAg \end{Bmatrix}$; this precipitate

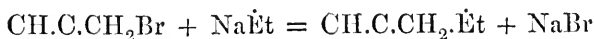
may, by means of acids, be reconverted into allylene. Iodine withdraws likewise the silver, and forms $C_3H_3I = CI.C.CH_3$. This iodide is not acted on by ammonia, solution of potash, sodium, or ethylate of sodium, but the iodine is easily expelled by nascent hydrogen and allylene reproduced. Also $CAg.C.CH_3$ does not exchange its silver with ethylic iodide even at $150^\circ C$. From these properties it appears that the hydrogen in allylene which may be replaced by silver or iodine cannot be supplanted by the residues of water, alcohol, or ammonia.

The bromide of bromopropylene $C_3H_5Br_3 = CH_3.CBr_2.CH_2Br$ and tribromide of allyl, respectively, are acted on by potassic ethylate in the following manner:—As in the case of propylenic bromide, two molecules of hydrobromic acid are withdrawn from the compounds, but the third atom of bromine is exchanged for the alcohol residue $C_2H_5O = \dot{E}t$. It is on account of this similarity existing in the behaviour of this last atom of bromine and the bromine in ethylic bromide that the group CH_3 must be assumed as a proximate constituent of allylene. Acetylene $CH.CH$ does not show this reaction:



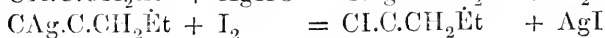
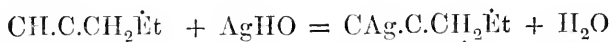
Bromide of bromopropylene.

Allylenic bromide.

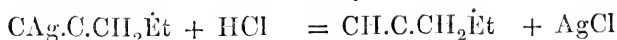


Allylenic bromide.

If sodic methylate, instead of sodic ethylate, is made to act on $C_3H_5Br_3$, a corresponding methyl-compound is obtained. These ethers have still the properties of allylene; an atom of hydrogen may first be replaced by silver or by iodine. Thus:—



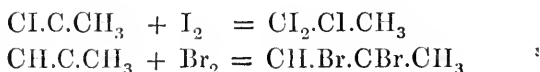
and finally



Ether of allylene.

Allylene contains two chemical units less than propylene, and,

accordingly, it can combine with two atoms of a monatomic element and form bodies belonging to the propylene group:*



If it is remembered that in all compounds consisting of carbon, hydrogen, and oxygen, and which may be considered as derivatives of a given hydrocarbon, the oxygen can only be contained either as a substitute for hydrogen or in the form of the water-residue $\dot{\text{H}}$, it is at once seen that it is possible to draw up a complete list of all such derivatives. Assuming that propylic hydride consists of the three groups $\text{CH}_3.\text{CH}_2.\text{CH}_3$, that all hydrogen-atoms are of the same chemical value, and that $\dot{\text{H}}$ can occur only once in each of the residues, I obtain for the oxygen-derivatives of propylic hydride the list on pages 286 and 287:—

In the first part of this paper it has been pointed out that the group $\text{CH}_2\dot{\text{H}}$ imparts alcoholic properties to compounds consisting of carbon, hydrogen, and oxygen, when it occurs as one of their proximate constituents, and that glycol is a diatomic alcohol because it contains this group twice. If a compound contains, besides carbon and hydrogen, only the residue $\dot{\text{H}}$, it comports itself like an n -atomic alcohol in case $\dot{\text{H}}$ occurs n times in it. It was also shown that COH causes organic bodies to behave like acetic aldehyde, and that acid properties are owing to the presence of the group COH . An n -basic acid contains this group n times.† Different combinations of these three groups in the same body give compounds of a mixed character. Glycollic acid $\text{CH}_2\dot{\text{H}}.\text{COH}$, for example, possesses the properties of an alcohol and acid, and glyoxylic acid $\text{COH}.\text{COH}$ those of an aldehyde and acid. There occurs also in the ethylic hydride group an oxide analogous to an anhydrous inorganic oxide, ethylenic oxide = $\left\{ \begin{array}{l} \text{CH}_2\text{O} \\ \text{CH}_2 \end{array} \right.$.

The foregoing remarks apply also to the different members of the propylic hydride group. In addition, the following is worthy of notice:—If the residue $\dot{\text{H}}$ replaces an atom of hydrogen in group CH_2 of a hydrocarbon, a pseudo-alcohol, and if the two atoms of hydrogen in CH_2 are replaced by an atom of oxygen, a

* Ann. Ch. Pharm. cxxxi, 123; cxxxv, 266; cxxxiii, 121; cxxxv, 272; Jahresbericht, 1864, 494.

† Chem. Soc. J. [2] iv, 23, 24, 26, 27, 28.

TABLE II.—Propylic Hydride = $\text{CH}_3\text{CH}_2\text{CH}_3$.

Empirical Formulae.	Rational Formulae.				
$\text{C}_3\text{H}_8\text{O}$	1 $\text{CH}_3\text{CH}_2\text{CH}_2\text{H}$ Propylic alcohol.	2 $\text{CH}_3\text{CHH}\cdot\text{CH}_3$ Pseudo-propylic alcohol.			
$\text{C}_3\text{H}_8\text{O}_2$	3 $\text{CH}_3\text{CHH}\cdot\text{CH}_2\text{H}$ Propyl-Glycol.	4 $\text{CH}_2\text{H}\cdot\text{CH}_2\text{CH}_2\text{H}$			
$\text{C}_3\text{H}_8\text{O}_3$	5 $\text{CH}_2\text{H}\cdot\text{CHH}\cdot\text{CH}_2\text{H}$ Glycerin.				
$\text{C}_3\text{H}_6\text{O}$	6 $\text{CH}_3\text{CH}_2\cdot\text{COH}$ Propionic aldehyde.	7 $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ Acetone.	8 $\left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH} \\ \text{CH}_3 \end{array} \right\} \text{O}$ Propylenic oxide.		
$\text{C}_3\text{H}_6\text{O}_2$	9 $\text{CH}_3\text{CH}_2\cdot\text{COH}$ Propionic acid.	10 $\text{CH}_3\text{CHH}\cdot\text{COH}$	11 $\text{CH}_2\text{H}\cdot\text{CH}_2\cdot\text{COH}$	12 $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{H}$	13 $\left\{ \begin{array}{c} \text{CH}_2 \\ \text{CH} \\ \text{CH}_2 \end{array} \right\} \text{O}$
$\text{C}_3\text{H}_6\text{O}_3$	14 $\text{CH}_3\text{CHH}\cdot\text{COH}$ Lactic acid β	15 $\text{CH}_2\text{H}\cdot\text{CH}_2\cdot\text{COH}$ Lactic acid α	16 $\text{CH}_2\text{H}\cdot\text{CHH}\cdot\text{COH}$	17 $\text{CH}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\text{H}$	

$C_3H_4O_4$	¹⁸ $CH_2H.CHH.CO\dot{H}$ Glyceric acid.	²⁰ $COH.CH_2COH$	²¹ $\left\{ \begin{array}{c} CH_3 \\ CH \\ CO \end{array} \right\} O$ Lactide.	²² $\begin{array}{c} CHO \\ CH \\ CH_2 \end{array} \left\} O\right.$	²⁷ $\left\{ \begin{array}{c} CO \\ CH \\ CH_2H \end{array} \right\} O$	²⁸ $\left\{ \begin{array}{c} COH \\ CH \\ CH_2 \end{array} \right\} O$
$C_3H_4O_2$	¹⁹ $CH_3.CO.CO\dot{H}$					
$C_3H_4O_3$	²³ $CH_3.CO.CO\dot{H}$ Pyruvic acid?	²⁴ $CH_2H.CO.CO\dot{H}$	²⁵ $COH.CH_2.CO\dot{H}$	²⁶ $COH.CHH.CO\dot{H}$		
$C_3H_4O_4$	²⁹ $CH_2H.CO.CO\dot{H}$	³⁰ $COH.CH_2.CO\dot{H}$ Malonic acid.	³¹ $COH.CHH.CO\dot{H}$			
$C_3H_4O_3$	³² $CO\dot{H}.CHH.CO\dot{H}$ Tartronic acid.					
$C_3H_4O_4$	³³ $COH.CO.CO\dot{H}$	³⁴ $\left\{ \begin{array}{c} COH \\ CH \\ CO \end{array} \right\} O$				
$C_3H_4O_4$	³⁵ $CO\dot{H}.CO.CO\dot{H}$	³⁶ $\left\{ \begin{array}{c} CO \\ CH \\ COH \end{array} \right\} O$				
$C_3H_4O_5$	³⁷ $CO\dot{H}.CO.CO\dot{H}$ Mesoxalic acid.					

ketone results,—thus, we have pseudo-propylic alcohol and acetone in the propylic hydride group, two bodies which cannot possess representatives in the ethylic hydride group.

The body marked (4) in Table II, is isomeric with propyl-glycol, but has not yet been prepared. It contains CH_2H twice, and no doubt possesses the properties of a diatomic alcohol. Glycerin (5), with three residues H , is a triatomic alcohol. Propionic aldehyde (6) owes its similarity to acetic aldehyde to the group COH , and propylenic oxide (8) is homologous to and has the same constitution as ethylenic oxide. In monobasic propionic acid (9) we meet the group COH once. The bodies represented by the formulæ placed under the numbers (10), (11), (12), and (13) are not known; (10) is the formula of the first aldehyde of propyl-glycol, (11) an aldehyde of glycol (4), (12) stands to propyl-glycol as acetone does to pseudo-propylic alcohol, and (13) is epichlorhydrin in which the chlorine has been replaced by H . (14) and (15) show the constitution of the two lactic acids, and indicate by the groups COH , CIIH , and CH_2H , their acid and alcoholic properties. (16) and (17) represent two aldehydes of glycerin; (16) is perhaps the formula of propyl-phycite. Glyceric acid is monobasic and triatomic, as indicated by its formula under (18). (19) is probably the aldehyde of pyruvic acid, and (20) occupies in the propylic the same position as glyoxal does in the ethylic hydride group. (21) represents lactide, and (22) the aldehyde of glycide. Pyruvic acid possesses probably the formula given under (23); (24) represents the second aldehyde of glycerin; (25) is homologous to and has the same constitution as glyoxylic acid. (26) is the formula of another aldehyde of glycerin which contains still one of the residues H , and therefore ought to possess, besides the properties of an aldehyde, also those of an alcohol. (27) stands to lactide like ethylic alcohol to ethylic hydride, and (28) would be an acid related to glycide like glyceric acid to glycerin. The acid formed by the action of argentic oxide on chloropropionic acid is most probably represented by (29); (30), with its two groups COH , stands for bibasic malonic acid; and (31) is related to glyceric acid like glyoxylic acid to glycollic acid. Tartronic acid, as is seen by its formula (32), is bibasic and triatomic; (33) is an aldehyde of mesoxalic acid, and (34) of the acid under (36); (35) stands to mesoxalic as glyoxylic does to oxalic acid, and therefore ought to possess the properties of an aldehyde and an acid.

Nearly half the substances mentioned in Table II are not known,

but I doubt not that all will be prepared in course of time. Eight of the nine oxygen derivatives, which are theoretically possible in the ethylic hydride group, are known, whereas only seventeen of the thirty-seven compounds which theory predicts for the propylic hydride group, have, up to the present time, been described.

$\text{CH}_3.\text{CH}_2.\text{CH}_3$ is distinguished from $\text{CH}_3.\text{CH}_3$ by the group CH_2 which it contains, in addition to $\text{CH}_3.\text{CH}_3$. The introduction of this group impresses on the oxygen derivatives of the hydrocarbon C_3H_8 some features that are wanting in those of the homologous body C_2H_6 .

If an atom of hydrogen in the group CH_2 is replaced by the water-residue H , pseudo-propylic alcohol $\text{CH}_3.\text{CHH}.\text{CH}_3$ results. There can be no doubt that the abnormal properties of pseudo-amylic alcohol are due to the same cause. Amylene possesses probably the formula $\text{CH}_3.2\text{CH}_2.\text{CH}.\text{CH}_2$, and pseudo-amylic alcohol would be accordingly $\text{CH}_3.2\text{CH}_2.\text{CHH}.\text{CH}_3$, whereas amylic alcohol must be represented thus:— $\text{CH}_3.3\text{CH}_2.\text{CH}_2\text{H}$. Oxidising agents attack, as a rule, first the hydrogen in that group in which the water-residue is contained. Therefore, it is clear that to a pseudo-alcohol no normal aldehyde, nor an acid with the same number of carbon-atoms as the alcohol, can correspond, because the group CHH cannot be converted into COH or COH without the destruction of the molecule. In the case of pseudo-propylic alcohol, acetone $\text{CH}_3.\text{CO}.\text{CH}_3$, and in that of pseudo-amylic alcohol, the ketone $\text{CH}_3.2\text{CH}_2.\text{CO}.\text{CH}_3$ must be formed. Kolbe appears to have obtained this body. If the action of oxidising agents is continued, the ketones are by degrees broken up into bodies of simpler composition, until at last only carbonic acid and water remain. Wurtz obtained from pseudo-amylic alcohol, pseudo-butylic alcohol, acetone, acetic acid, and carbonic acid.*

Benzhydrolet† and β -hexylic alcohol‡ are also pseudo-alcohols. Analogy justifies the conclusion that the hydrocarbons, homologous with propylene and higher up in the series, are represented by the general formula $\text{CH}_3.n\text{CH}_2.\text{CH}.\text{CH}_2$, and furnish, like propylene and amylenes, pseudo-alcohols, the water-residue attaching itself to the group CH .

* Ann. Ch. Pharm. Oct. 1864, 105. Ibid. 132.

† Ann. Ch. Pharm. Jan., 1865, 11.

‡ Ann. Ch. Pharm. Aug., 1865, 146.

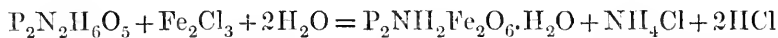
XXVI.—*Notes on Pyrophosphodiamic Acid.*

By J. H. GLADSTONE, Ph.D., F.R.S.

SINCE the paper of the late Mr. Holmes and myself, in which the formula of Pyrophosphodiamic acid was established,* I have made several new observations on this body. I propose throwing them together under the three headings of Characteristic Test, Methods of Preparation, and Compounds.

Characteristic Test.

The ready formation of ferric pyrophosphamate from an acid solution of a pyrophosphodiamate affords a very good test for this substance. If it be an insoluble salt that is to be examined, it should be dissolved or decomposed by cold dilute sulphuric acid; and, if a solution, it should be rendered strongly acid, with sulphuric acid if possible, but other acids will answer the purpose though they are more likely to destroy the compound sought for. To this acid solution a few drops of a ferric salt should be added; sufficient to colour it distinctly red. On heating this mixture the presence of pyrophosphodiamic acid is shown by the appearance of a haziness in the warmer currents, which soon extends itself over the whole liquid, and the ferric pyrophosphamate separates in small white flocculent masses. If the acid be present in large quantity, the liquid will become gelatinous. As far as I know, no other ferric compound of a similar appearance can be produced by heating any very acid solution, but the fact of the precipitate being really the pyrophosphamate may be further proved by its solubility in ammonia. Occasionally the precipitate will not form till the mixture is fairly boiling. The reaction which takes place may be thus expressed:—



But the question arises, Is there no other compound that will give the pyrophosphamate under similar circumstances? There are anides of pyrophosphoric acid which contain a larger amount of the elements of ammonia, and these do give the same reaction; but

* Chem. Soc. J. xvii, p 225.

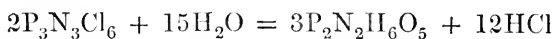
whether in doing so they pass through the intermediate stage of the diamic acid it is impossible to say. Thus the weak aqueous solution which is obtained when pyrophosphotriamic acid is treated with hot water gives this reaction; but there is little fear of confounding the triamic with the diamic acid, on account of the almost insolubility of the one, and the extreme solubility of the other. There exist, however, two substances, or two modifications of the same substance, intermediate in composition between the diamic and triamic acids, which yield the ferric pyrophosphamate with the greatest facility. It is necessary, therefore, to have some means of distinguishing these. Their salts seem in general less soluble than the pyrophosphodiamates; but there is a much more trustworthy means of recognition, and one that has the advantage of being applicable to quantitative separation. Pyrophosphodiamic acid is very soluble both in water and in alcohol, but the higher compounds, though water dissolves them freely, are thrown down from their aqueous solution on the addition of common spirits of wine. The alcoholic solution may be tested for the diamic acid by the iron test, but it should be diluted with about an equal volume of water before it is heated, so as to ensure a sufficiently high temperature to effect the transformation into the pyrophosphamate.

Methods of Preparation.

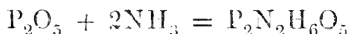
The reactions by which pyrophosphodiamic acid is produced are very numerous; indeed, there would seem to be a great tendency in the elements to arrange themselves in this particular form. Most of the processes, however, give at the same time a larger or smaller quantity of the higher compound which is insoluble in alcohol.

In the papers already referred to the following three methods were pointed out:—

1st. By decomposing chlorophosphuret of nitrogen with an alcoholic solution of an alkali, or even by the slow action of water.



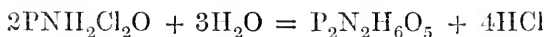
2nd. By saturating phosphoric anhydride with dry ammonia-gas.



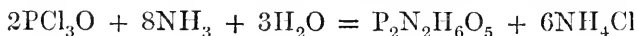
3rd. By acting on oxychloride of phosphorus with dry ammonia at a low temperature. Two molecules of ammonia are absorbed, as is shown by the increase of weight—about 22 per cent. ; and I have reason to believe that the resulting white solid mass is a mixture of chloride of ammonium and an amidated oxychloride. The following will be the expression of this first stage of the reaction :—



which on the addition of water splits up thus :—



The last two methods of producing this acid may be modified in a way which saves time and trouble, namely, by using the strongest aqueous ammonia, sp. gr. 0·880, instead of the dry gas. Thus phosphorus may be burnt in a large vessel containing some ammonia at the bottom. In this case there is a white substance produced which is insoluble in water or acids, and which renders the solution milky, and is very difficult to separate from the liquid containing the pyrophosphodiamate of ammonium. Again, oxychloride of phosphorus may be dropped continuously into aqueous ammonia, when pyrophosphodiamic acid is produced, perhaps without the intervention of the amidated oxychloride—



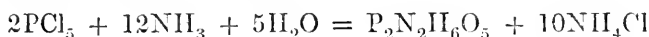
Akin to this last method is the following :—

4th. By throwing pieces of pentachloride of phosphorus into the strongest aqueous solution of ammonia. The reaction is very violent, and it is desirable to cool the vessel in which it is performed. An insoluble white flocculent substance appears in small quantity, which gives reactions characteristic of pyrophosphotriamate of ammonium, while the solution made decidedly acid, and heated with a ferrie salt, gives the ferrie pyrophosphamate. This is due to a mixture of pyrophosphodiamic acid and the higher compound. It is hardly credible that no phosphoric acid is produced, but the magnesium test fails to detect any in the tribasic condition.

This experiment was performed quantitatively. 0·65 grm. of pentachloride of phosphorus gave 0·035 grm. of pyrophosphotriamate of ammonium, and 0·305 grm. of ferrie pyrophosphamate.

Phosphorus as pyrophosphotriamate..	0.0113	gm.	or 11.7 %
„ „ pyrophosphamate	0.0762	„	78.9 „
Loss.....	0.0091	„	9.4 „
	<hr/>		
Original phosphorus.....	0.0966	„	100.0

A considerable part of this small loss must be due to the escape of dense fumes on bringing the two bodies into contact. The main reaction seems to be—

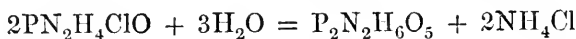


If the solution of ammonia be not very strong, phosphate and chloride of ammonium are the only products.

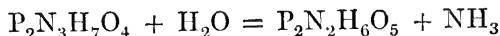
5th. By saturating oxychloride of phosphorus with dry ammonia-gas at 100°C ., or thereabouts. It then takes up four molecules, and on the addition of water there is formed a mixture of the insoluble triamic with the soluble diamic acid, and generally a large quantity of the intermediate compound. The production of the pyrophosphodiamic acid probably takes place in these two stages:—



and



6th. By boiling for a long time a solution of pyrophosphotriamic acid in water, especially if some hydrochloric acid be present.

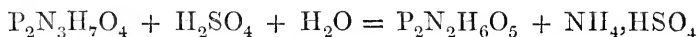


This is an intermediate step in the reduction of the amide to phosphoric acid.

7th. By treating the acid intermediate in composition between the triamic and the diamic acid with a large amount of some other acid, even acetic; or by decomposing its salts with a strong acid.

8th. By dissolving pyrophosphotriamic acid or a pyrophosphotriamate in sulphuric acid, either quite strong or mixed with a very small quantity of water. Heat is required to effect the solution, and it must not be continued long, lest the action proceed too far. The acid solution diluted with water and neutralized, gives no precipitate, showing that the pyrophosphotriamic acid is really

decomposed, while it gives the ferric pyrophosphamate only on boiling.



9th. By heating pyrophosphotriamic acid to 250°C ., and treating the resulting mass with water. There are other products of decomposition.

10th. By dissolving in strong sulphuric acid the substance obtained by saturating oxychloride of phosphorus with dry ammonia at 300°C ., and washing the resulting mass with water. The body thus formed differs from pyrophosphotriamic acid, and on analysis gave numbers very different from Schiff's phosphamide (phosphotriamide). It requires the assistance of heat to dissolve it, and apparently stronger acid than is needed in the case of pyrophosphotriamic acid.

11th. By heating Gerhardt's phosphamide with sulphuric acid.



Compounds.

It has already been shown that pyrophosphodiamic acid is bibasic, the silver-salt, for instance, being $\text{P}_2\text{N}_2\text{H}_4\text{Ag}_2\text{O}_5$, or $\text{P}_2(\text{NH}_2)_2\text{Ag}_2\text{O}_5$. In such a case it would be likely enough that compounds should be obtained in which only one of the two atoms of hydrogen is replaced by a metal, or in which a part of the remaining hydrogen is so replaced, as with the triamic acid. I have not, however, succeeded in forming any other silver-salt; but the barium-salt produced in different ways is certainly not uniform in composition, and one portion of it is often much more soluble in hydrochloric acid than another portion. Still I have never isolated any definite salt other than the bimetallic $\text{P}_2\text{N}_2\text{H}_4\text{Ba}_2\text{O}_5$.

Ammonium-salt. In my first paper on this subject* there are some experiments recorded which enable us to determine the composition of the ammonium-salt. A known weight of chlorophosphuretted of nitrogen was decomposed by an alcoholic solution of ammonia, and the resulting salts were evaporated to dryness in a water-bath, and weighed. As nothing is, or ought to be, pro-

* Chem. Soc. Qu. J. iii, 360.

duced in this reaction except the chloride and pyrophosphodiamate of ammonium, it is easy to reckon the amount of alkaline base which has entered into combination.

I.	0.2135	gram.	of $P_3N_3Cl_6$	yielded	0.387	gram.	of salts.
II.	0.2553	„	„	„	0.469	„	„
III.	0.7035	„	„	„	1.2505	„	„

These numbers are in the proportion of

I.	100 : 181.2
II.	100 : 183.7
III.	100 : 177.7

and they indicate that the pyrophosphodiamate of ammonium produced contained 2 molecules of the base and was therefore $P_2N_2H_4(NH_4)_2O_5$, which theoretically should give an increase of 100 : 182.8.

Metallic Salts.—According to the notes of Mr. Holmes, a neutral solution of mixed pyrophosphodiamate and chloride of ammonium gives with soluble salts of silver barium and zinc, the bimetallic salts that have been analysed; with chloride of strontium and calcium, white flocculent precipitates, readily soluble in acids, but insoluble in ammonia; with chloride of cadmium and manganese similar white precipitates, soluble both in acids and ammonia; with chloride of copper and of nickel blue flocculent precipitates, and with chloride of cobalt a similar violet compound, all soluble either in ammonia or acids. All these precipitates are believed to be, more or less, soluble in chloride of ammonium. It was found at the same time that no precipitate was given with solutions of corrosive sublimate, ferric or chromic sulphate, alum, sulphate of magnesium, or the tartrate of potassium and antimony.

I may also add that a slightly acid solution of pyrophosphodiamic acid gives a white flocculent precipitate with a solution of lead, and a more granular precipitate with a solution of tin, both of which are easily dissolved by nitric acid. The uranic compound is exceedingly soluble in acids, and is dissolved like the oxide by carbonate of ammonium.

Acid.—In recent experiments, pyrophosphodiamic acid has never been obtained in a crystalline form, as stated in my original paper; and I believe that when pure it closely resembles phosphoric acid itself in its physical properties.

Ether.—In the same paper I described an aromatic oil, which makes its appearance when chlorophosphuret of nitrogen is decomposed in the presence of ether or alcohol. It was concluded from its products of decomposition that this liquid is deutazophosphoric (pyrophosphodiamic) ether. Later observations have served to confirm this view ; but no quantitative analysis has recently been made. The only determination of the carbon and hydrogen was unsatisfactory, since a large quantity of unburnt charcoal or hydrocarbon was found after the combustion in the bulb that had been used to contain the liquid. However, notwithstanding this loss, there was obtained 14·4 % of carbon and 4·5 % of hydrogen, which indicates more than 1 molecule of ethyl, and leads to the belief that the compound was probably $P_2N_2H_4(C_2H_5)_2O_5$, which, if completely burnt, should have given 20·6 % of carbon, and 6 % of hydrogen.

XXVII.—*Researches on the Phosphates of Calcium, and upon the Solubility of Tricalcic Phosphate.*

By ROBERT WARINGTON, Junr.

THE original object of this investigation was to ascertain the solubility of the phosphates of calcium employed in agriculture, more particularly under the conditions to which they would be subject after mixture with the soil. Other points of interest soon, however, arose in the course of experiment ; the subject thus spread beyond its intended limits, and in the present communication the agricultural part of the question is left still very incomplete.

The plan proposed, was to determine, in the first place, the solubility of pure, artificially prepared phosphates, and next the solubility, under similar circumstances, of the impure phosphates available for agriculture. Tricalcic phosphate was chosen as the first subject of experiment ; its preparation in the pure state was thus a primary object.

Mitscherlich tells us, that when chloride of calcium is added to ordinary disodic phosphate, the latter being maintained in excess, the precipitate formed is tricalcic phosphate, while the solu-

tion becomes acid from the production of monosodic phosphate. Berzelius, on the contrary, states, that the precipitate formed under these conditions is not tricalcic phosphate, but the octocalcic triphosphate, which he has elsewhere described. All experimenters agree, that when the operation is reversed, and disodic phosphate is poured into an excess of chloride of calcium, the precipitate is neither tricalcic nor octocalcic, but dicalcic phosphate.

In following out Mitscherlich's plan, very different results were obtained to those which he describes; a series of experiments was therefore instituted as to the result of mixing disodic phosphate and chloride of calcium.

I. A solution of ordinary disodic phosphate was slowly poured into pure chloride of calcium. The turbidity occasioned by the first drops of the sodium-salt disappeared on agitation;* on a further addition the precipitate soon became permanent, and the solution at the same time distinctly acid. On standing, the precipitate became decidedly crystalline, while the surface of the liquid was covered with floating crystals; these when examined under the microscope were found to have the form of rhombic prisms. The chloride of calcium had been maintained in excess throughout the experiment. The precipitate was thoroughly washed by decantation. On drying it appeared as a crystalline powder, possessing a somewhat nacreous lustre. Analysis yielded the following results:—

EXPERIMENT 1.—*a.* 5.05 grains of the ignited salt gave 4.11 grs. CaCO_3 , and 4.27 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

b. 10.52 grs., gave 8.50 grs. CaCO_3 .

c. 4.88 grs., gave 13.30 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$.

EXPERIMENT 2.—Another specimen prepared in an exactly similar manner to the above. A portion of the moist precipitate was redissolved; it gave 7.41 grs. CaCO_3 , and 7.84 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

	Theory.	Experiment I.			Experiment II.
		<i>a.</i>	<i>b.</i>	<i>c.</i>	
2CaO	44.10	45.58	45.25	—	45.28
P ₂ O ₅	55.90	54.08	—	54.27	54.72
	<hr/>	<hr/>			<hr/>
	100.00	99.66			100.00

The salt was therefore dicalcic phosphate, containing, however, an excess of lime, amounting to rather more than 1 per cent.

* According to H. Rose, dicalcic phosphate is slightly soluble in chloride of calcium.

The methods of analysis employed were twofold. As they are the same as were used throughout the investigation, a short description seems necessary. In the first method the lime was precipitated by oxalate of ammonium from an acetic acid solution of the phosphate, the filtrate concentrated, and the phosphoric acid precipitated by magnesia. In using this method, a correction was always made for the bulk of the filtrate and washings from the magnesia precipitate, .008 gr. being added to the weight of $\text{Mg}_2\text{P}_2\text{O}_7$ for each ounce of fluid. The amount of lime obtained in this plan of analysis appears to be a little above the truth, the error apparently amounting to 1—3-tenths per cent. of the precipitate. Qualitative analysis showed that it contained a trace of phosphoric acid.

The second method consisted in the precipitation of the phosphoric acid by acetate of uranium, the precipitate being washed, by decantation, with hot water containing a little acetate of ammonium, then dried, ignited, and weighed.

II. We have seen that the result of adding disodic phosphate to an excess of chloride of calcium is the formation of dicalcic phosphate; we now turn to the next experiment, in which chloride of calcium was added to an excess of disodic phosphate.

As disodic phosphate possesses a distinct alkaline reaction, it is evident that the precipitate first formed on addition of chloride of calcium, must originate under alkaline conditions. As, however, more of the calcium-salt is added, this alkaline reaction disappears, and the fluid finally becomes acid. The precipitates obtained in the operation are thus formed under a variety of circumstances. The attempt was made to examine separately the phosphates produced at the different periods of the reaction.

EXPERIMENT 1.—The chloride of calcium was added in such quantity that the fluid remained distinctly *alkaline* after standing. A portion of the washed precipitate, redissolved, gave 3.92 grs. CaCO_3 and 3.12 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 2.—Another specimen, prepared as above, gave 2.71 grs. CaCO_3 and 2.12 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 3.—Chloride of calcium added so that the solution after standing appeared perfectly *neutral*. A portion of the washed precipitate gave 5.08 grs. CaCO_3 and 4.15 grs. $\text{Mg}_2\text{P}_2\text{O}_7$:

	Theory.	I. alkaline.	II. alkaline.	III. neutral.
8CaO	51.26	52.37	52.80	51.73
3P ₂ O ₅	48.74	47.63	47.20	48.27
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Tricalcic phosphate contains 54.19 per cent. of lime.

It appears then that the precipitate produced when the phosphate of sodium was used in greatest excess, was not tricalcic phosphate, but more nearly approached in composition the octocalcic triphosphate of Berzelius, the proportion of lime being, however, somewhat excessive; and that when the chloride of calcium was used in rather larger quantity, the liquid after standing being neutral, not alkaline, the composition of the precipitate approached still more nearly to this formula.

The nature of the precipitate, formed after the solution became *acid*, next engaged attention.

Chloride of calcium was poured into phosphate of sodium till the liquid became faintly acid; the clear solution was then decanted and the addition of the calcium continued. The precipitate which now fell was highly crystalline, and formed streaks on the side of the beaker wherever the stirring rod had passed. On standing, the sides of the vessel were covered with small crystals. The salt thus obtained was washed and analysed.

A portion of the moist precipitate, redissolved, gave 3.69 grs. CaCO₃ and 3.97 grs. Mg₂P₂O₇.

	Theory.	Experiment (acid solution).
2CaO	44.10	44.86
P ₂ O ₅	55.90	55.14
	<hr/> 100.00	<hr/> 100.00

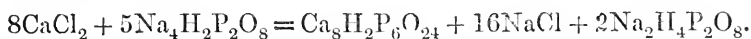
There can be no doubt from this proportion, that the crystalline precipitate from the acid solution was dicaleic phosphate. As analysis showed the salt to be nearly pure, a water-determination was further made.

8.73 grs. of the vacuum-dried salt, lost on ignition 2.30 grains, or 26.35 per cent.; the formula Ca₂H₂P₂O₈.4H₂O, demands 26.16 per cent. of water. Dried at 100° the salt contained 23.72 per cent. of water; less than one equivalent was therefore lost at this temperature. The composition of this salt is exactly that of

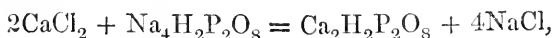
Boedeker's phosphate. According to Raewsky,* the salt prepared as above contains one equivalent less water than that found in the present case.

It appears then, that when chloride of calcium is gradually added to a solution of disodic phosphate, the precipitate first formed is octocalcic triphosphate; and this reaction continues until the solution becomes acid; the precipitate after this ceases to be octocalcic, and becomes dicalcic phosphate.

The origin of the acid reaction is evident. Octocalcic phosphate can only be produced by the simultaneous formation of monosodic phosphate:



The cause of the acid reaction observed when disodic phosphate is poured into chloride of calcium is not so evident. If the calcium-salt formed be nothing but dicalcic phosphate, the reaction is simply:



and the formation of an acid phosphate is not admitted. I believe the true explanation lies in the acid character of dicalcic phosphate. If this salt in its moist condition is examined by delicate litmus paper, the reaction is always found to be faintly acid, however thoroughly it may have been washed. When we remember that this salt is dissolved to a considerable extent in the liquid during its formation, a part of the precipitate distinctly crystallising out, we shall, I think, allow that we have here a sufficient explanation of the phenomenon.

It is interesting to observe that while disodic phosphate is of an alkaline nature, dicalcic phosphate possesses faint acid properties. When dicalcic phosphate is boiled in water, the solution becomes strongly acid; according to Boedeker† the salt is decomposed under these circumstances, and both monocalcic and tricalcic phosphate are produced.

The crystalline form of the dicalcic tetrahydrated phosphate has been examined by Professor Church. He describes the crystals as thin rhomboidal plates, of which the diagonally opposite acute angles are sometimes truncated, hexagonal forms being thus produced. This truncation seems to be occasionally

* Compt. rend. xxvi, 205.

† Quoted, Storer, Diet. Solubilities, in loco.

hemihedral, and then may proceed up to the diagonal between the obtuse angles; from this change triangular forms arise. Other modifications are also met with.

When dicalcic phosphate, freshly precipitated and washed, is treated with solution of disodic phosphate, the crystalline character of the precipitate disappears, and it becomes octocalcic triphosphate. In an experiment in which the phosphate of sodium was renewed several times, and left in contact some days, the resulting salt had the composition 52.02 per cent. CaO and 47.98 per cent. P_2O_5 .

III. The next experiment was an attempt to convert dicalcic phosphate into the tricalcic salt by dissolving it in hydrochloric acid and pouring the solution into excess of ammonia.

EXPERIMENT 1.—Solution of dicalcic phosphate reprecipitated by pouring into ammonia—4.26 grs. of the ignited salt gave 3.95 grs. $CaCO_3$ and 3.18 grs. $Mg_2P_2O_7$.

EXPERIMENT 2.—Solution of a phosphate containing 47.96 per cent. CaO, reprecipitated by ammonia—4.34 grs. gave 3.99 grs. $CaCO_3$ and 3.28 grs. $Mg_2P_2O_7$.

	Theory.	I.	II.
8CaO	51.26	51.92	51.48
3P ₂ O ₅	48.74	47.75	48.34
	<hr/> 100.00	<hr/> 99.67	<hr/> 99.82

The salt obtained was thus octocalcic triphosphate. The ammonia had failed to convert the dicalcic phosphate into tricalcic.

To test the decomposing power of the ammonia to its utmost, the salt obtained in Experiment 1, was again redissolved and poured into strong ammonia. The washed precipitate was analysed with the following result—

a. 8.80 grs. of the ignited salt gave 7.99 grs. $CaCO_3$ and 6.64 grs. $Mg_2P_2O_7$.

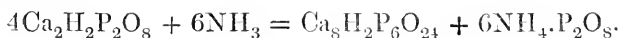
b. 5.93 grs. gave 14.28 grs. $2U_2O_3.P_2O_7$.

	Theory.	a.	b.	a. recalculated to 100 parts.
8CaO	51.26	50.84	—	51.30
3P ₂ O ₅	48.74	48.26	48.00	48.70
	<hr/> 100.00	<hr/> 99.10	<hr/>	<hr/> 100.00

The octocalcic phosphate was thus unaltered by ammonia. Berzelius has a statement to the same effect.

We may then safely affirm that whenever dicalcic phosphate,

octocalcic triphosphate, or any phosphate of intermediate composition, is precipitated from solution by ammonia, the salt obtained will be the octocalcic triphosphate; a tricalcic phosphate cannot be obtained in this manner. The following is probably a type of the reaction:—



Professor Church suggested at an early period of the research that the octocalcic triphosphate written by Berzelius Ca_8P_6 , doubtless contained water of constitution. The following experiments were made on the specimen last described.

2·64 grains, vacuum-dried, lost on ignition ·255 grs., or 9·65 per cent. The formula $\text{Ca}_8\text{H}_2\text{P}_6\text{O}_{24}\cdot 4\text{H}_2\text{O}$, requires 9·34 per cent of water.

33·28 grs., dried at 100° for several days, lost on ignition 1·79 grs., or 5·37 per cent. The formula $\text{Ca}_8\text{H}_2\text{P}_6\text{O}_{24}\cdot 2\text{H}_2\text{O}$, demands 5·81 per cent.

In the last experiment, the salt continued to lose weight very slowly in the water-bath; a part of the two equivalents of water is thus apparently removed at this temperature.

It might seem probable, that this phosphate, formed in an ammoniacal solution, would contain no water of constitution but ammonia in its place; unlike, however, the magnesium-salt produced in similar conditions, this is not the case.

Octocalcic triphosphate may of course be written $2\text{Ca}_3\text{P}_2\text{O}_8\cdot\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8$.

Octocalcic triphosphate is neutral to litmus, or acid to the faintest possible degree; on boiling with water, the solution becomes strongly acid.

IV. We shall now turn to the experiments relating to tricalcic phosphate.

Tricalcic phosphate may of course be prepared by adding trisodic phosphate to any neutral solution of calcium. The phosphate employed in the determinations of solubility was made either by adding one equivalent of caustic ammonia to a known amount of ordinary phosphate of sodium, and pouring this solution into chloride of calcium: or by simply mixing a considerable excess of ammonia with the phosphate of sodium, and adding chloride of calcium in quantity not quite sufficient to precipitate all the phosphoric acid. Berzelius, indeed, states that the latter method, when phosphate of ammonium is employed, yields only octocalcic phosphate; and the direction he

gives for preparing this salt is to add ammonia to diammonic phosphate, and then precipitate half the phosphoric acid with chloride of calcium.* Yet we have on his own authority, that when ammonia is added to diammonic phosphate, *triammonic phosphate* separates as a crystalline magma if the solutions are strong. If then, the addition of an excess of ammonia converts the diammonic into triammonic phosphate, how can the subsequent addition of chloride of calcium fail in producing a tricalcic phosphate?

The following are analyses of tricalcic phosphate prepared by different methods:—

EXPERIMENT I.—Disodic phosphate, plus one equivalent of ammonia, poured into chloride of calcium — 9.89 grs. of ignited salt gave 9.32 grs. CaCO_3 and 6.77 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 2.—Salt prepared as above—9.88 grs. gave 9.32 grs. CaCO_3 and 6.79 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 3.—Excess of ammonia added to disodic phosphate, and chloride of calcium poured in, but not in excess. A portion of the moist precipitate gave 7.34 grs. CaCO_3 and 5.40 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 4.—Salt prepared as in No. 3; only half the phosphoric acid precipitated. A portion of the moist precipitate gave 10.06 grs. CaCO_3 and 7.44 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 5.—A large excess of ammonia added to diammonic phosphate; chloride of calcium then added in quantity sufficient to precipitate only a very small part of the phosphoric acid. A part of the washed precipitate gave 11.12 grs. CaCO_3 and 8.32 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 6.—Salt prepared as No. 5; a somewhat larger proportion of chloride of calcium used, yet less than half the phosphoric acid precipitated. A specimen of the washed precipitate gave 8.75 grs. CaCO_3 and 6.32 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

	Theory.	I.	I. Recalculated to 100 parts. †	II.	II. Recalculated to 100 parts. †	III.	IV.	V.	VI.
$3\text{CaO} \dots$	54.19	52.77	54.65	52.83	54.58	54.33	54.25	53.90	54.78
$\text{P}_2\text{O}_5 \dots$	45.81	43.78	45.35	43.96	45.42	45.67	45.75	46.10	45.22
	100.00	96.55	100.00	96.79	100.00	100.00	100.00	100.00	100.00

* Of course, if chloride of calcium were poured into diammonic phosphate, and ammonia *afterwards* added, the octocalcic triphosphate would result. Berzelius' direction is however explicit, that the ammonia is to be added *before* the chloride of calcium.

† Though all the phosphates were washed by decantation till no chlorine was

The phosphate produced in each of these experiments was thus tricalcic phosphate. Phosphate of ammonium, after mixing with excess of ammonia, is seen to have produced tricalcic phosphate when partially precipitated by chloride of calcium.

A determination of water was made in the specimen obtained in experiment No. 4. 6.72 grs. of the vacuum-dried salt lost, on ignition, .69 grs. or 10.26 per cent.; the formula $\text{Ca}_3\text{P}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$, demands 10.40 per cent. of water. Dried at 100° till it ceased to lose weight, the salt still contained 6.35 per cent. of water; less than one equivalent was therefore lost at this temperature.

This experiment agrees with the determination of Berzelius, who states the amount of water to be two equivalents.

Tricalcic phosphate is neutral to litmus paper; if, however, it be boiled with water, the solution becomes distinctly acid. This is a strange reaction, and invites investigation. We have indeed seen that on boiling dicalcic and octocalcic triphosphate, the same phenomenon occurs; with these, however, the formation of an acid salt admits of ready explanation, while in the case of tricalcic phosphate, the splitting up into a basic and an acid salt is certainly hard to understand.

If acetic or hydrochloric acid is poured on moist tricalcic phosphate in such quantity that a small portion of the salt is left undissolved, the solution, if filtered, will deposit crystals of dicalcic phosphate; while the residue left undissolved by the acid will be converted into the same salt, and on standing assume its characteristic crystalline form. The crystals are larger when acetic acid has been made use of; indeed, by following this method, crystals of considerable size may be obtained.

Having narrated the experiments which were made as to the preparation, the composition, and properties of the phosphates of calcium, we arrive now at the experiments touching the solubility of tricalcic phosphate; the trials to be here related deal exclusively with the pure, freshly precipitated phosphate.

It is quite possible that precipitated tricalcic phosphate may possess somewhat different solubilities, when prepared by different methods; this difference can, however, scarcely be great. The present experiments are at all events comparable with each other,

found in the washings, the analysis in several cases failed to reach 100 parts. In determinations of solubility the portion of precipitate taken was always submitted to several additional washings.

all having been made with similarly prepared phosphate, and most of them from the same specimen, the analysis of which has been given in Section IV Experiment 4.

It will be seen in every case that the solubility has been determined by precipitation of the phosphoric acid with uranium; the solubility is thus reckoned from the amount of *phosphoric acid* dissolved. The uranium method was adopted as admitting of immediate use, without previous removal of lime; and also because the great weight of the uranium renders the estimation of small quantities of phosphoric acid comparatively easy.

V. The first experiment was upon the solubility of tricalcic phosphate in pure water. As the presence of carbonic acid is known to increase the solubility of this salt, the precaution was taken of boiling the distilled water for some time before use. The phosphate and water were allowed to digest in the cold for several days, with occasional agitation; the solution was then filtered, a weighed amount of the filtrate evaporated to a small bulk, and the phosphoric acid determined by uranium.

EXPERIMENT 1.—Tricalcic phosphate with boiled water, 6 days; temperature when filtered, $8\cdot2^{\circ}$.—18,000 grains of solution gave $\cdot50$ grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or $\cdot2173$ grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 82,823.

EXPERIMENT 2.—Residue from above with boiled water, 6 days; temperature on removing solution 6° .—18,000 grs. gave $\cdot41$ grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or $\cdot1782$ grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was thus 1 in 101,010.

EXPERIMENT 3.—Tricalcic phosphate and boiled water, 10 days; temperature when filtered $6\cdot2^{\circ}$.—18,000 grs. gave $\cdot49$ grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or $\cdot213$ grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 84,515.

The solubility of tricalcic phosphate in pure water is thus seen to be quite insignificant, the mean of the three experiments being 1 in 89,449.

The solution of tricalcic phosphate gives after some time a faint precipitate with oxalate of ammonium. The phosphoric acid can, however, be immediately detected, either by nitrate of silver, acetate of uranium, or by Fresenius' iron-test; the last is indeed a most delicate reaction for phosphoric acid. Ammonia produces no change in the solution.

When a considerable quantity of the solution of tricalcic phosphate is evaporated almost to dryness, the concentrated fluid will

be found to have a distinct acid reaction. This decomposition of the phosphate has been already noticed.

VI. The next determination was the solubility in a solution of chloride of ammonium. The presence of ammonium-salts has been long known to increase the solubility of tricalcic phosphate; few definite results seem, however, to have been published. The subject possesses an agricultural interest, since a part of the effect of ammonium-salts as manure, is thought by some to be due to their solvent power for phosphates.

The chloride of ammonium in these experiments was dissolved in boiled water; care was taken to neutralize with ammonia the slight acid reaction which chloride of ammonium usually possesses.

EXPERIMENT 1.—Tricalcic phosphate in 1 per cent. solution of chloride of ammonium, 20 days*; temperature when filtered 11° .—18,052 grs. of solution gave 2.08 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or .904 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 19,969.

EXPERIMENT 2.—Tricalcic phosphate in 1 per cent. chloride of ammonium, 20 days; temperature when filtered, 12.3° .—18,052 grs. of solution gave 2.17 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or .943 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 19,143.

EXPERIMENT 3.—Another specimen of tricalcic phosphate in 1 per cent. chloride of ammonium, 11 days; temperature when filtered 7° .—18,052 grs. of solution gave 2.10 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or .9128 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was thus 1 in 19,776.

EXPERIMENT 4.—Tricalcic phosphate in 10 per cent. solution of chloride of ammonium, 16 days; temperature when filtered, 17.3° .—8235 grs. of solution gave 4.38 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 1.904 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 4325.

The results of these trials give a mean solubility of 1 in 19,629, in a 1 per cent. solution of chloride of ammonium; and a solubility of 1 in 4325 in a 10 per cent. solution of this salt. The addition of the ammonia salt had thus greatly increased the solvent power of the water.

The solution in chloride of ammonium is not rendered turbid by ammonia, unless the quantity added is considerable; the phosphate is at the best only very imperfectly precipitated.

Neither phosphate of sodium nor chloride of calcium produces any precipitate when employed alone, but if added with ammonia,

* The long periods mentioned here, and in other places, were not generally the result of choice, but convenience.

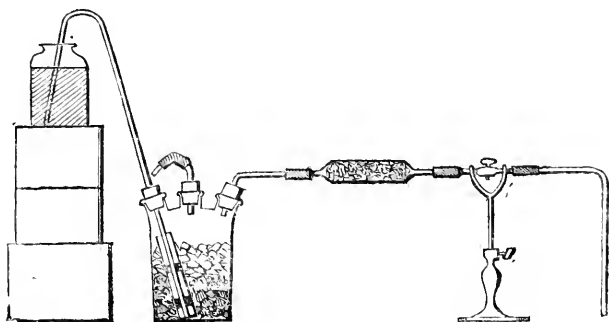
nearly the whole of the tricalcic phosphate is precipitated. Thus an ammoniacal solution containing an alkaline phosphate will never contain more than a trace of lime, however great may be the amount of ammoniacal salt present; and the converse is true, though to a less degree, of an ammoniacal solution containing an excess of lime.

VII. We now pass to the solubility of tricalcic phosphate in water saturated with carbonic acid gas. Boussingault has abundantly shown that carbonic acid gas exists in field soils to a considerable extent, and especially where the organic matter is large in quantity; the solvent power of water holding this gas in solution becomes therefore an important item in soil economy.

The experiments under this head were made in the following manner. The phosphate, diffused through water, was contained in a pint bottle, which it nearly filled, and carbonic acid was made to bubble slowly through the mixture. The passage of the gas produced sufficient motion to keep the phosphate in suspension.

The apparatus used for generating a constant stream of gas was constructed from an ordinary Woulfe's bottle. As the apparatus admits of easy construction, and was found to answer well, it may be worth while describing.

A Woulfe's bottle, of about 30 ozs. capacity, is furnished through one of its necks with a syphon of considerable height; the short leg of the syphon is outside the bottle, and dips into a vessel of strong hydrochloric acid. The bottom of the Woulfe's bottle is filled with pumice, or pieces of broken earthenware; upon the pumice is placed a quantity of broken marble; the centre neck of the bottle is fitted with an india-rubber tube terminating in a



glass stopper. The remaining neck is connected with a wide tube filled with fragments of chalk (to purify the gas from hydrochloric acid), beyond which is placed a glass stop-cock and delivery tube.

Suppose the stop-cock closed, then on removing the stopper from the tube in the central neck, and applying suction with the lips, the syphon will be filled. The stopper is then replaced, and, if the apparatus be tight, the acid remains stationary in the syphon. On now opening the cock of the delivery tube, air passes out; the acid descends the syphon, rises through the pumice, and immediately attacks the marble; but only just the quantity of gas is produced which the position of the stop-cock allows to escape, for when more is evolved, the pressure on the surface of the acid forces it to descend to a lower level, and pass up the syphon to the acid reservoir. A constant stream of gas is thus obtained of almost any required rapidity.

When the apparatus is no longer required, the stop-cock is closed, the acid reservoir lowered, and the bottle emptied of acid by pressure from the lips applied to the tube attached to the central neck.

The limb of the syphon within the Woulfe's bottle is surrounded by an outer tube to prevent small bubbles of gas from entering the syphon. Fresh acid and marble are readily supplied as wanted.

The solutions in carbonic water were brought on to the filter by means of a glass syphon provided with a stop-cock, fitted by a cork into the neck of the bottle containing the liquid to be filtered. The filter was carefully covered to hinder access of air.

EXPERIMENT 1.—Tricalcic phosphate in water; carbonic acid passed ten hours; height of barometer at the end of the operation 29·034 inches;* temperature when filtered 5·3°†. 8095 grs. of solution gave 10·36 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 4·503 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1797.

EXPERIMENT 2.—Tricalcic phosphate in water; gas passed fourteen hours; height of barometer at the end of the operation 30·136 inches; temperature when filtered, 9·3°. 7281 grs. of solution gave 10·04 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 4·364 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1668.

* The height of the barometer has been corrected for temperature in every case.

† Unfortunately the temperature was not registered at the time of passing the gas, save in a few cases only; the degrees mentioned above refer to the temperature of the solution when filtered the following day.

EXPERIMENT 3.—Tricalcic phosphate in water; gas passed fourteen hours; height of barometer 29·082 inches; temperature when filtered, 9·3°. 8075 grs. of solution gave 9·80 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 4·26 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1895.

EXPERIMENT 4.—Residue from preceding experiment treated as before; gas passed twelve hours; height of barometer 29·887 inches; temperature on filtering, 7·3°. 8044 grs. of solution gave 10·30 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 4·477 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1796.

The mean of these experiments gives a solubility of 1 in 1789, at a mean pressure of 29·535 inches, and a temperature of *about* 10°.*

According to Bischof, the solubility of moist tricalcic phosphate in carbonic water is 1 in 1102. Liassaigne, as the result of one experiment, gives the solubility as 1 in 1333 at the temperature of 10° and ordinary pressure.

I will just note, that in an experiment with a phosphate which had been dissolved and re-precipitated, a solubility as high as 1 in 1540 was obtained. The barometer in this experiment stood at 30·136 inches; the temperature was *about* 12°. The conditions were, indeed, precisely the same as those of Experiment 2.

The solution of tricalcic phosphate in carbonic water possesses a slight acid reaction. The addition of ammonia only occasions a faint milkiness. Disodic phosphate produces an immediate precipitate. Chloride of calcium is without effect.

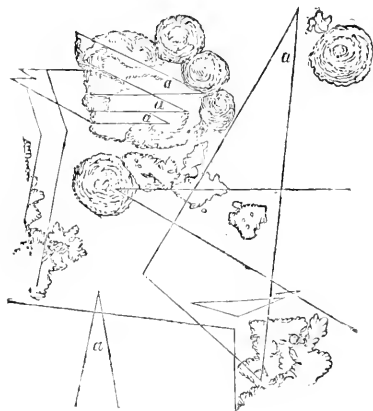
When the solution is heated, no considerable precipitation of phosphate takes place till the temperature has reached about 80°; the precipitation is then very sudden.† A large proportion of the carbonic acid may thus be expelled without separating the phosphate. Strong solutions naturally become clouded at a lower temperature than weaker ones.

If the solution of tricalcic phosphate in carbonic water be exposed to air at common temperatures, a crystalline film is formed on the surface after some hours. The crystals were examined under the microscope, and found to agree in form with tetrahydrated dicalcic phosphate. If the crystalline film when fully developed is separated by filtration, and the solution again allowed

* The room becoming warmer towards the end of the day, the temperature when the gas † as last passed would be a little greater than the temperature of the solution when filtered on the following morning.

† The boiling was conducted in a flask nearly filled by the solution.

to stand, no more crystals of dicalcic phosphate are deposited, but the film is composed entirely of a net-work of small botryoidal masses. If this film be also removed, the next deposit will be found to contain another new form, consisting of comparatively large globular aggregations. This form survives the reticulations, and continues to be deposited as long as any film is produced. If the carbonic solution of tricalcic phosphate is allowed to stand some days, all three forms may be found in one film.



I am indebted to Professor Church's kindness for the sketch which accompanies the present description, and also for much help in the microscopical observations. The sketch represents a film containing all three forms; the reticulated substance is however somewhat imperfectly developed. The crystals marked *a* are those of dicalcic phosphate.

During the slow deposit of these various substances, the fluid loses its acid reaction and becomes alkaline to red litmus. I think I may state, that no dicalcic crystals are formed after the solution has acquired an alkaline reaction.

An attempt was made to identify the various forms by analysis; the quantity operated on being necessarily very small, the results must be taken with some reservation.

A crust composed mainly of dicalcic crystals, but containing a little of the reticulated form, gave .35 grs. CaCO_3 , and .37 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or 45.36 per cent. of lime and 54.64 per cent. of phosphoric acid, a composition nearly approaching dicalcic phosphate.

A later crust, made up of the reticulated and globular forms, gave .44 grs. CaCO_3 , and .37 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or 51.01 per cent. of lime, and 48.99 per cent. of phosphoric acid, a proportion almost exactly that of octocalcic triphosphate.

A still later crust, composed mainly of the globular body, gave .59 grs. CaCO_3 , and .45 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or 53.44 per cent. of lime, and 46.56 per cent. of phosphoric acid; a proportion approaching that of tricalcic phosphate.

These analyses, I think, establish the fact, that the crystals first formed are dicalcic phosphate, but the precise nature of the two other forms remains uncertain; we only see that each successive crust contains a greater proportion of lime than the preceding, and that the last, composed mainly of the globular body, has apparently reached the condition of tricalcic phosphate. The reticulated form is probably an octocalcic or heptocalcic triphosphate.

When the solution of the phosphate has ceased to produce crusts by exposure to air, a certain amount of solid matter still remains in solution, and is deposited on boiling. A solution which had ceased to form a deposit, even at a summer temperature, was concentrated by evaporation and analysed in the ordinary way; it gave $\cdot 60$ grs. CaCO_3 , and $\cdot 18$ grs. $\text{Mg}_2\text{P}_2\text{O}_7$; or per cent. 74.50 parts of lime, and 25.50 parts of phosphoric acid. There was, therefore, as might naturally be expected, a considerable excess of lime left in the solution. This most likely existed as carbonate; indeed we shall see further on, that a solution of carbonate of calcium in carbonic acid possesses, like this solution, a distinctly alkaline reaction; a perfect proof is, however, wanting.

The decomposition of tricalcic phosphate during the evaporation of its carbonic solution, is perfectly analogous to the decomposition of the same phosphate already referred to as taking place in its acetic and hydrochloric solutions. Dicalcic phosphate, in either case, crystallises out, while the solution retains the excess of lime.

The formation of several distinct deposits from a carbonic solution during its exposure to air is interesting in a geological aspect, as it seems very probable that by a similar action a variety of mineral substances may be produced by the action of carbonic water on one or two simple compounds.

VIII. The next series of experiments was upon the solvent power of ammonium-salts in the presence of carbonic acid gas.

EXPERIMENT 1.—Tricalcic phosphate in 1 per cent. chloride of ammonium solution; gas passed 10 hours; height of barometer 29.034 inches; temperature when filtered, 6.8° . 8122 grs. of solution gave 14.14 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or 6.146 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1321.

EXPERIMENT 2.—Tricalcic phosphate as above; gas passed 12 hours; height of barometer 29.663; temperature when filtered 12.3° . 7649 grs. of solution gave 12.77 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or 5.55 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was thus 1 in 1377.

The mean solubility from these experiments will be 1 in 1349, at a pressure of 27·348, and a temperature of about 12°.

The addition of chloride of ammonium greatly increased the solubility in pure water; its addition to water saturated with carbonic acid has produced comparatively small result. As Experiment 1 was made under precisely the same circumstances as the first experiment in Section VII., the exact effect of the ammonium-salt can be calculated. We find, then, that for 100 dissolved by the ammonium-solution, 73·5 were dissolved by the pure carbonic water.

On heating the solution of phosphate no deposit takes place till the thermometer reaches about 88°. The chloride of ammonium, though dissolving more, thus holds the phosphate longer in solution than pure carbonic water.

IX. The next point experimented on was the influence of certain ingredients of soil upon the solubility of phosphate of calcium; and first of limestone. What effect would the presence of limestone in a soil have upon the solubility of tricalcic phosphate? The first trial was concerning the amount of pure carbonate of calcium which water saturated with carbonic acid was capable of dissolving.

The quantity of carbonate dissolved in the aerated water was determined by boiling the carbonic solution, adding hydrochloric acid, evaporating the whole fluid in a platinum basin, then treating with excess of sulphuric acid, and, after ignition, weighing the sulphate of calcium obtained.

EXPERIMENT 1.—Precipitated undried carbonate of calcium in water; gas passed 20 hours; height of barometer at time of last passing, 29·226 inches; temperature when filtered, 18·6°. 8000 grs. of solution gave 10·55 grs. of CaSO_4 , or 7·757 grs. CaCO_3 . The solubility was therefore 1 in 1031.

EXPERIMENT 2.—Carbonate of calcium in water as before; gas passed 24 hours; height of barometer, 29·700 inches; temperature at *last* passing of gas, 21·3°. 8010 grs. of solution gave 10·87 grs. CaSO_4 , or 7·993 grs. CaCO_3 . The solubility was therefore 1 in 1002.

The mean of these two experiments gives the solubility of carbonate of calcium as 1 in 1016; the height of the barometer being 29·463 inches, and the temperature about 21°.

Bischof tells us that in his experiments the maximum solubility was, at ordinary pressures, 1 in 1000, a result very close to that here obtained.

The solution of carbonate of calcium in carbonic water has a faint alkaline reaction to red litmus, becoming very marked as the paper dries. Ferric oxide is precipitated when perchloride of iron is dropped into the solution, and in other respects it behaves as a weak alkali. These alkaline properties doubtless play an important part in geological transformations.

The carbonate of calcium is of course precipitated from solution when caustic soda or ammonia is added to the liquid; but I was not prepared to find that alkaline carbonates, and even bicarbonates, produced a similar effect. The precipitation with bicarbonate of potassium, or sodium, is not so immediate as with carbonate of sodium, but after a few minutes is apparently as complete.

The carbonic solution of carbonate of calcium does not become turbid when heated, till the temperature has reached about 80° .

X. We pass to the experiments in which tricalcic phosphate was mixed with carbonate of calcium, thus imitating the conditions which occur when a phosphatic manure is applied to a limestone soil.

As both substances were used in the undried state, it was difficult to mix them in any definite proportion; the quantities mentioned are thus only rough approximations.

EXPERIMENT 1.—Tricalcic phosphate, with at least twice its weight of carbonate of calcium, in water; gas passed several days; height of barometer at last passing of gas, 29.881; temperature at same time 19.3° . 7266 grs. of solution evaporated to dryness with slight excess of acetic acid; the residue, after ignition, weighed 8.17 grs. The mass, redissolved, gave .48 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or .208 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility of the phosphate was therefore 1 in 31,932.

EXPERIMENT 2.—The undissolved residue from previous experiment treated as before; gas passed 22 hours; height of barometer 29.754 inches; temperature when filtered, 19° . 7035 grs. of solution gave .36 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or .156 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility of the phosphate was thus 1 in 45,096.

The results here obtained make it evident, that where an excess of carbonate of calcium exists, the amount of tricalcic phosphate dissolved by carbonic water is excessively small; the water becomes saturated with carbonate of calcium, while only a trace of the phosphate enters into solution. In the next experiment the proportion of the carbonate was much smaller.

EXPERIMENT 3.—Tricalcic phosphate and carbonate of calcium, the latter perhaps a twentieth of the former; gas passed 25 hours; height of barometer 29·692; temperature, last time of passing gas, 20·3°. 7741 grs. of solution gave ·38 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or ·165 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility of the phosphate was thus 1 in 46,915.

EXPERIMENT 4.—The undissolved residue from Ex. 3 again treated with water, and gas passed 4 hours; the clear liquid was then decanted off. Fresh water was poured on the solid matter, and gas passed for 4 hours; the solution thus obtained was also removed. The residue remaining after this repeated treatment with carbonic water, was put on again; gas passed for 25 hours; temperature of solution, when filtered, 13°. 7600 grs. of solution gave 6·19 grs. of $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 2·69 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility of the phosphate was thus 1 in 2825.

No appreciable amount of carbonate of calcium was present in the liquid.

We see here, first, that a comparatively very small amount of carbonate of calcium is sufficient to prevent the solution of tricalcic phosphate; next, we see the progressive action of a continued supply of water saturated with carbonic acid upon a mixture of phosphate and carbonate of calcium. At first the carbonate is dissolved, accompanied by only a trace of phosphate; as the action progresses, the carbonate is gradually removed from the mixture; and then, and not till then, the phosphate freely enters into solution.

The bearing of these facts on the chemistry of soils is obvious. Phosphate of calcium will be dissolved by the aerated water of a calcareous soil to only a minute extent, and a phosphatic manure applied to such a soil will be only very slowly diffused throughout it; at least these are the natural deductions from the experiments, supposing always that there are not unknown interfering influences in the conditions of a natural soil.

We may in the same manner conclude, that manures like bone-ash, or coprolite, containing both carbonate and phosphate of calcium, will yield their greatest fertilising effect some time after their application; the solubility of the phosphate becoming greater as the carbonate of calcium is removed.

XI. An experiment was made as to the effect of chloride of ammonium upon the mixture of tricalcic phosphate and carbonate of calcium.

EXPERIMENT 1.—Tricalcic phosphate, with excess of carbonate of calcium, in 1 per cent. solution of chloride of ammonium; gas passed 12 hours; height of barometer 29·378 inches; temperature when filtered 14·3°. 8061 grs. of solution gave 1·00 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or ·4346 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The amount of phosphate dissolved was thus 1 in 18,552.

The chloride of ammonium in this instance has more than doubled the solvent power of the carbonic water.

XII. It was thought that, possibly, the influence of the ammonium-salt in the last experiment might be simply due to a capacity for dissolving carbonate of calcium, owing to which, the liquid never became saturated with this substance; the amount of this salt soluble in chloride of ammonium under the influence of carbonic acid, was therefore determined.

EXPERIMENT 1.—Carbonate of calcium in 1 per cent. solution of chloride of ammonium; gas passed 12 hours; height of barometer 29·425 inches; temperature when gas last passed 13·3°. 8134 grs. of solution gave 11·65 grs. CaSO_4 , or 8·566 grs. CaCO_3 . The solubility was therefore 1 in 950.

This proportion is but slightly greater than that previously found for pure carbonic water.

The solution obtained in this experiment did not deposit carbonate of calcium when heated, nor even on long boiling. H. Rose has shown that carbonate of calcium is readily dissolved by a boiling solution of chloride of ammonium, of course with decomposition of the latter.

XIII. The last of the present experiments, was upon the influence of hydrated ferric oxide and alumina on the solubility of phosphate of calcium. As both ferric oxide and alumina are insoluble in water, they can scarcely be expected to prevent the solution of a phosphate: at the same time, by their superior affinity for phosphoric acid, they might succeed in decomposing the phosphate when dissolved, and remove the phosphoric acid from solution.

The plan of the experiment was as follows. Three equal volumes of a solution of tricalcic phosphate in carbonic water were taken; in one, the amount of lime and of phosphoric acid were determined; to the others were added hydrated ferric oxide and hydrated alumina, respectively. Then after digestion for some days, carbonic acid being passed from time to time to maintain a saturated solution, the liquid was filtered, the residue

washed with carbonic water, and the lime and phosphoric acid in the filtrate determined.

EXPERIMENT 1.—8000 grs. of a solution of tricalcic phosphate in carbonic water was found to contain 2·54 grs. $\text{Ca}_3\text{P}_2\text{O}_8$, or 1·163 grs. P_2O_5 and 1·377 grs. CaO .

EXPERIMENT 2.—To 8000 grs. of the above solution was added some well washed precipitated ferric oxide, and carbonic acid passed from time to time. After two weeks the liquid was separated; it yielded to analysis 2·46 grs. CaCO_3 , or 1·377 grs. CaO , and ·08 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, equal to ·051 grs. P_2O_5 . The ferric oxide was dissolved in hydrochloric acid, and the phosphoric acid it contained determined; it gave 1·74 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or 1·113 grs. P_2O_5 .

EXPERIMENT 3.—8000 grs. of the same solution with freshly precipitated hydrate of alumina, the operation conducted as above. The solution gave 2·35 grs. CaCO_3 , or 1·316 grs. CaO , and ·06 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, equal to ·038 grs. P_2O_5 . The alumina yielded to analysis 1·24 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or ·793 grs. P_2O_5 .*

It appears then, that both hydrated ferric oxide and hydrated alumina have the power of decomposing phosphate of calcium very perfectly in a carbonic acid solution. At the end of the action, the whole of the lime remains dissolved as carbonate, while the phosphoric acid has been abstracted and is now combined with the iron or aluminum. In the experiment with oxide of iron, 95·7 per cent. of the phosphoric acid was thus absorbed; with the alumina the absorption was 96·8 per cent.† There are many analogies to this action; the separation of phosphoric acid from its solutions by oxide of tin, and the absorption of arsenious acid by hydrated ferric oxide, will at once suggest themselves.

Viewed agriculturally, this reaction is very important. There are few soils in which ferric oxide is not a considerable ingredient, and it undoubtedly exists chiefly in a hydrated condition; the presence of uncombined alumina is perhaps more problematic. Now will not the oxide of iron in a soil have the same effect on

* The whole of the phosphoric acid was not recovered from the alumina, owing to an unforeseen analytical difficulty.

† Dr. Voelcker states, in one of his papers, that oxide of iron and alumina decompose a solution of monocalcic phosphate, and that tricalcic phosphate, and phosphate of iron, or of aluminium is produced. The present experiments go further and show that these hydrated oxides are, in the presence of carbonic acid, capable of completely decomposing a basic phosphate, and combining with the whole of its phosphoric acid.

the phosphate of calcium applied in manure as the oxide of iron had in the experiment just considered? As the phosphate of the manure is dissolved and brought in contact with the soil, will not the phosphoric acid be abstracted and become phosphate of iron, while the lime percolates through the soil dissolved in carbonic water?

If this be so, the solubility of phosphate of iron under various conditions becomes of equal importance with the solubility of phosphate of calcium. Fresh light too is thrown on the phenomenon of the absorptive power of soils; a property which is held by some to depend on mere surface attraction, and to be therefore, analogous to the decolorising faculty of charcoal, but which, if these results are borne out by actual experiment on soil, is, at least in the case of phosphoric acid, of a purely chemical nature.

We commenced by saying that the agricultural part of the investigation was as yet very imperfect. I hope on a future occasion to be able to throw some further light on the subject.

Subjoined is a tabular view of the various solubilities determined. Where several experiments have been recorded, the mean only is given.

EXPERIMENTS WITH TRICALCIC PHOSPHATE.

Nature of Solid.	Nature of Fluid.	Pressure. (inches).	Temperature. (centigrade)	Parts of fluid containing 1 part of Tricalcic Phosphate.
Tricalcic phosphate	Boiled water	7°	89,449
Tricalcic phosphate	1 % Chloride of ammonium in boiled water	10°	19,629
Tricalcic phosphate	10 % Chloride of ammonium in boiled water	17°	4,325
Tricalcic phosphate	Carbonic saturated water	29.535	10°	1,789
Tricalcic phosphate	1 % Chloride of ammonium in carbonic saturated water	29.348	12°	1,352
Tricalcic phosphate, plus carbonate of calcium ..	Carbonic saturated water	29.776	21°	42,314
Tricalcic phosphate, plus carbonate of calcium ..	1 % Chloride of ammonium in carbonic saturated water ..	29.378	16°	18,552

EXPERIMENTS WITH CARBONATE OF CALCIUM.

Nature of Solid.	Nature of Fluid.	Pressure. (inches).	Temperature. (centigrade)	Parts of fluid containing 1 part of Carbonate of Calcium.
Carbonate of calcium	Carbonic saturated water	29.463	21°	1,016
Carbonate of calcium	1 % Chloride of ammonium in carbonic saturated water ..	29.425	13°	950

XXVIII.—*On the Preparation of Chrysammic Acid.*

By JOHN STENHOUSE, LL.D., F.R.S., &c., and HUGO MÜLLER, Ph.D., F.R.S., &c.

THE preparation of chrysammic acid is both troublesome and tedious. We think, however, that the following will be found more advantageous than any of the processes which have hitherto been published. Although at first sight this process may appear complicated, yet it is not more so than is necessary to obtain a good result; for if the action of the nitric acid be not pushed far enough, the large quantity of aloetic acid and resinous matter unconverted is a great hindrance to the purification of the chrysammic acid; whilst, on the other hand, if the action be continued too long, much of the chrysammic acid is destroyed. Six parts by measure of nitric acid, sp. gr. 1.36, are placed in a large retort connected with a good condensing arrangement, and when heated nearly to boiling, two parts of socotrine aloes broken into small pieces are gradually added. The action is very violent, large quantities of nitrous fumes being given off, so that at the commencement of the operation, the aloes must be added slowly, and little or no heat applied. When, however, a considerable quantity has been introduced, it will be found necessary to heat, in order to accelerate the action, and the acid which distils over should be poured back into the retort at intervals. When the whole of the aloes is in the retort, the digestion is continued for about ten hours, during the last three of which the weak acid may be distilled off, so that the contents of the retort are reduced to one-half of their original volume. To this residue three measures of nitric acid are gradually added, and the digestion is continued for about six or seven hours, distilling off the bulk of the acid during the latter part of the digestion. The residue in the retort is now poured into about four parts of water, and after agitation the undissolved picric and aloetic acids,—separated by this means from the oxalic acid produced in the reaction,—are collected, and when dry, or nearly so, introduced into a retort with one part of strong nitric acid, sp. gr. 1.45, and digested in the manner previously described for six or eight hours. The residue, which now consists of picric, aloetic, and chrysammic acids, is washed by decantation with successive quantities of boiling water, until the washings become of a

pink colour, instead of the deep orange which they had at first. By this means the picric acid is removed. The mixture of chrysammic and aloetic acids thus obtained is dried and returned to the retort with one part more of strong nitric acid, and digested as above for ten hours, by which means most of the aloetic acid is converted into chrysammic acid.

It is now washed with hot water until the washings have a pink colour, and then boiled for a few minutes with about four parts of water and filtered. This operation is repeated three or four times, until the colour of the filtrate is bright red instead of purple.

It is then again boiled with water, and a slight excess of chalk added, when the contents of the flask become of a deep-red or purple colour. On cooling, minute red needles of chrysammate of calcium may be seen on the side of the flask, also a flocculent mass of them at the bottom. These should be collected, dried, and crystallised from dilute spirit—equal parts of alcohol and water. If the aloes have not been sufficiently acted upon, and a considerable quantity of aloetic acid is present, these needles do not crystallize out the first time, but by boiling with fresh quantities of water, and leaving the liquid to cool between each operation, they at last make their appearance, the aloetate of calcium which seems to prevent their crystallisation being removed, as it is much more soluble in cold water than the chrysammate. The red washings, &c., obtained in these various operations, when strongly acidulated with nitric acid, yield a considerable quantity of crude aloetic acid, which may be converted into chrysammic acid by further treatment with strong nitric acid. By this process aloes yield from three to four per cent. of chrysammate of calcium. Although aloes is the most convenient source, yet considerable quantities of chrysammic acid may be economically made by treating with nitric acid the resin of aloes left undissolved in the preparation of cold extract of aloes. Though this resin yields but little more than half the amount that aloes itself does, yet being a waste product, it is an advantageous source of the acid. As already mentioned in a short paper by Warren de la Rue and Hugo Müller on some derivatives of chrysophane (*Zeitschrift f. Chemie*, 1862),* chrysammic acid is also the product of the action

* In this paper the authors point out the probable connection which exists between chrysophane and chrysammic acid; the latter being the only product of the action of fuming nitric acid on chrysophane. It might, therefore, be considered as tetranitro-

of nitric acid on chrysophane and some other constituents of rhubarb.

Chrysammate of Calcium.



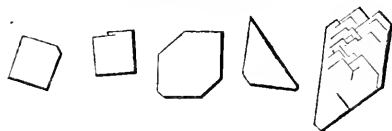
The crude chrysammate of calcium obtained by the above process is purified by crystallising several times alternately from boiling water and spirit. The clear red solution of the pure salt in boiling water forms on cooling a magma of bright red needles, which contract considerably on drying. It is very soluble in boiling alcohol, moderately so in boiling water, from which it crystallises out almost entirely on cooling. When dried *in vacuo*, it loses water, and becomes of a chocolate colour, but on exposure to the air, it quickly absorbs moisture and regains its original bright red colour. At 145° it is anhydrous, and when analysed gave the following results:—

I. 1.021 grammes gave .224 grm. carbonate of calcium.

		Theory.	I.
$C_7N_2HO_6$	= 209	—	—
Ca	= 20	8.73	8.77
	<hr/> 229		

Messrs. Schunck and Mulder described the chrysammate of calcium, which they obtained as a dark-red, somewhat crystalline powder.

Chrysammic Acid.



On adding a slight excess of nitric acid to a concentrated chrysophane, and as such the formula of chrysammic acid would require to be doubled. The results of the analysis of chrysophane and chrysammic acid hitherto obtained do not however show sufficient accordance to justify already the adoption of their theory.

boiling solution of pure chrysammate of calcium, pure chrysammic acid is precipitated. When cold the acid may be collected, and forms golden scales of considerable size and great lustre, very much resembling iodide of lead in appearance. The filtrate is quite colourless, and does not contain a trace of chrysammic acid. When suspended in water, it decomposes neutral solutions of nitrate of copper, acetate of copper, sulphate of nickel, chloride of manganese, and other salts, even at ordinary temperatures. When dried at 100° and subjected to analysis, it gave the following results:—

I. .296 grm. gave .433 grm. carbonic acid, and .030 grm. water.

II. .2907 grm. gave .4323 grm. carbonic acid, and .0395 grm. water.

		Theory.	I.	II. (H. M.)
C ₇	= 84	40.00	39.90	40.57
N ₂	= 28	13.33	—	—
H ₂	= 2	.95	1.12	1.5
O ₆	= 96	45.72	—	—
	<hr/> 210	<hr/> 100.00		

Chrysammic acid, when digested with a mixture of chlorate of potassium and hydrochloric acid, is slowly decomposed into chloropierin, but without the formation of chloranil.

In the paper by Warren de la Rue and Hugo Müller, it is mentioned that when chrysammic acid is crystallised from glacial acetic acid, it takes up 21.5 to 21.6 per cent. of this acid, forming sealy prismatic crystals, which remain unchanged over sulphuric acid or caustic lime, but lose their acetic acid when heated above 100° C.

Benzoyl-chrysammic Acid.

Chrysammic acid, when heated together with chloride of benzoyl, takes up benzoyl, forming a yellow compound, which crystallises in the prismatic form, and is not acted upon at ordinary temperatures by carbonates or caustic alkalis, but when treated with alcoholic potash, is decomposed, with formation of chrysammate and benzoate of potassium. Benzoyl-chrysammic acid is nearly insoluble in most of the usual solvents.

Chrysammate of Magnesium.

This salt is easily obtained by boiling pure chrysammic acid with an excess of magnesia, or the carbonate, for some time, filtering, and leaving the liquid to cool, when the magnesium-salt crystallises out, if the solution be not too dilute, in very fine broad red plates, having great lustre. It is by far the most beautiful of the salts of chrysammic acid.

When heated on platinum-foil it decomposes with feeble explosion, throwing off the magnesia in a fine flocculent state, in the same manner that metallic magnesium does when burning.

Dried at 160° and subjected to analysis, it gave the following results :—

0.3215 grm. substance gave 0.0808 pyrophosphate of magnesium.

		Theory.	Analysis.
C_7	= 84	—	—
N_2	= 28	—	—
H	= 1	—	—
Mg''	= 12	5.43	5.38
O_6	= 96	—	—
	<hr/> 221		

Other Salts of Chrysammic Acid.

The *chrysammate of copper* is even more soluble in alcohol than the calcium-compound, and may be used with advantage in the preparation and purification of chrysammic acid. It forms prismatic crystals of considerable size.

The *manganese-salt* crystallises from a hot aqueous solution in large, but very thin, scaly crystals. Of all the chrysammates prepared, this salt possesses the most brilliant golden lustre. By transmitted light it is blood-red.

Most of the chrysammates exhibit a considerable degree of solubility in weak alcohol, and are obtained from this solvent in

distinct crystals, which, however, are generally very thin and scaly, so that their form cannot be ascertained with exactness. It has been observed that most of the salts of chrysammic acid are identical in form when examined under the microscope; generally they appear in the well known twin combinations so characteristic of gypsum.

Hydrochrysammide.

In addition to the processes already known for preparing this beautiful body, it may very readily be obtained by digesting pure chrysammic acid with zinc and a dilute acid, or by the action of hydriodic acid, to which a small piece of phosphorus has been added to prevent the separation of free iodine. Also on bringing chrysammic acid suspended in water in contact with sodium-amalgam, a purple solution containing hydrochrysammide is formed; and when this is shaken up in a well closed bottle with an excess of the amalgam, the purple colour soon changes into orange, but on admitting even the smallest amount of air, the purple colour is restored.

XXIX.—*On Chrysammic Ether.*

By JOHN STENHOUSE, LL.D., F.R.S., &c.

THIS ether is prepared by a process similar to that which I have previously described for styphnic ether, although it is much more difficult to obtain in a state of purity.

Pure chrysammic acid, obtained from chrysammate of calcium, is boiled with about twelve times its weight of water, and a concentrated solution of carbonate of sodium is added by degrees until the whole of the acid is dissolved, and the solution is slightly alkaline. Care should be taken to avoid any great excess of the carbonate, as it decomposes the chrysammic acid. When the chrysammate of sodium has completely crystallised out, which takes place in about 16 hours, it is collected and washed with a little cold water, and is rendered quite pure by re-dissolving in a small quantity of boiling water, filtering, and allowing to crystallise. The best method of obtaining the chrysammate of silver required for the preparation of the ether is to precipitate a solution of chrysammate of sodium in 50 parts warm water by a

slight excess of nitrate of silver, collect on a filter when cold, wash well with cold water, and dry at a gentle heat.

Chrysammic ether.—Chrysammate of silver prepared by the above process, and previously dried for half-an-hour at 100° , is introduced into a flask furnished with a long condensing-tube; five times its weight of dry iodide of ethyl is poured on it; and the whole is digested for 10 or 15 minutes in a water-bath. The long condensing-tube is now replaced by a bent one, and the excess of iodide of ethyl distilled off, leaving a residue of iodide of silver and chrysammic ether in the flask.

On digesting this with benzol, the latter is dissolved, and crystallises out on cooling in hard dark brown crystals. These are finely powdered and recrystallised four or five times from benzol until they assume a pale yellow colour. A final recrystallisation from alcohol renders them pure. In all these operations great care must be taken to avoid the presence of moisture, as otherwise the ether is partially decomposed, and its purification consequently rendered very difficult.

Pure chrysammic ether crystallises from spirit, in which it is not very soluble, in tough needles of a pale red colour. Out of benzol, in which it is tolerably soluble, it separates in the form of hard yellow prisms. It is nearly insoluble in bisulphide of carbon, and but slightly so in ether. When heated in a tube, it melts, but is at the same time decomposed. On platinum-foil it burns without deflagration.

The ether, crystallised from spirit and dried at 100° , gave the following results when subjected to analysis:—

I. .239 grm. substance gave .399 grm. carbonic acid and .056 grm. water.

II. .324 grm. substance gave .532 grm. carbonic acid and .075 grm. water.

		Theory.	I.	II.	Mean.
C ₉	= 108	45.37	44.79	45.54	45.16
N ₂	= 28	—	—	—	—
H ₆	= 6	2.52	2.57	2.60	2.58
O ₆	= 96	—	—	—	—
	<hr/>				
	238				

These results, as will be seen, agree very well with the formula $\left. \begin{array}{l} \text{C}_7\text{N}_2\text{HO}_5 \\ \text{C}_2\text{H}_5 \end{array} \right\} \text{O}$

XXX.—CONTRIBUTIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

1. *The Oxidation-products of the Propione produced from Carbonic Oxide and Sodium-ethyl.*

By J. ALFRED WANKLYN.

THE progress of research has shown that the various ketones are characterised by their oxidation-products. I have, accordingly, oxidized the propione which is obtained by the action of carbonic oxide on sodium-ethyl.

The mode of preparing this propione has been already described.* Before employing the propione, I submitted it to a careful fractionation, so as to remove the liquid of high boiling point which accompanies it in its crude state. It was distilled ten times, and then heated in a current of dry carbonic acid to expel traces of ether.

After this preparation, I sealed some of it in a tube, together with excess of bichromate of potash and dilute sulphuric acid, and heated the whole in the water-bath for several hours. On opening the tube, no gas escaped, showing that carbonic acid is not among the oxidation-products. Moreover, the contents of the tube had the well-known smell of the acetic acid series.

After distilling and re-distilling, a distillate was obtained free from sulphates. This distillate was treated with carbonate of baryta, which dissolved very readily. An excess of the carbonate was then added and the liquid boiled and filtered.

The resulting solution of baryta-salt was evaporated to dryness in the water-bath, and the residue dried at 110° C.

Baryta determinations were made.

I. 0.3922 gm. of the barium-salt was ignited, when it evolved abundance of organic matter, and gave .2804 gm. of carbonate of baryta. *Percentage of barium* = 49.77.

II. 0.6266 gm. of the barium-salt was precipitated with dilute sulphuric acid, and the resulting sulphate of barium separated by filtration, washed, dried, and ignited. The sulphate of barium weighed 0.5295 gm. *Percentage of barium* = 49.74.

* Chem. Soc. J. [2], iv, 13 (1866).

The theoretical percentages of barium in the propionate and acetate are exhibited as follows:—

Propionate.			Acetate.		
C ₃	36	—	C ₂	24	—
H ₅	5	—	H ₃	3	—
Ba	68·7	48·48	Ba	68·7	53·75
O ₂	32	—	O ₂	32	—
	<hr/>	<hr/>		<hr/>	<hr/>
	141·7	100·00		127·7	100·00

Thus the percentage of barium is seen to be intermediate between that required by propionate, and that required by acetate, of barium.

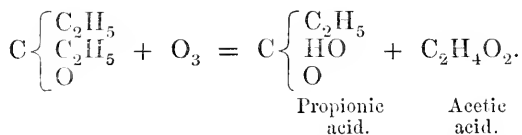
Some of the barium-salt was carefully tested for formiates, which proved to be absent. It is, therefore, certain that the barium-salt consisted in part of acetate. A portion of the barium-salt was decomposed with an equivalent of dilute sulphuric acid, and the organic acid thus obtained was about half saturated with carbonate of soda and distilled. From the distillate a barium-salt was made.

0·2066 grm. of this barium-salt gave, on ignition with sulphuric acid, 0·1728 grm. of sulphate of barium. Percentage of barium = 49·24, which approximates sufficiently to the number required by propionate of barium. It will be apparent that had there been higher acids present, a treatment of this kind would have furnished a barium-salt having an entirely different composition.

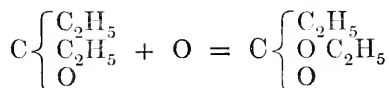
The sodium-salt resulting from this partial saturation was distilled with dilute sulphuric acid. The distillate had all the characters of acetic acid, giving cacodyl when a salt of it was heated with arsenious acid, and acetic ether on treatment with alcohol and concentrated sulphuric acid.

There is, therefore, no doubt that propione is resolved quite simply into propionic and acetic acids, when it is oxidized with bichromate of potash and dilute sulphuric acid. This is, I believe, the first example of a ketone being resolved into acids of less carbon-condensation than itself, without at the same time giving rise to carbonic acid.

The generation of propionic and acetic acids from propione without production of carbonic acid is quite in accordance with theory.



It is not improbable that the first stage of the process consists in the formation of propionate of ethyl, *e. g.*,



and that there should be great difficulty in arresting the progress of the oxidation so as to exhibit the ether. Be this, however, as it may, the connection between the mode of origin of propione, and the production of its oxidation, deserves remark. Formed directly from carbonic oxide and ethyl, it admits of oxidation into acetic acid—the oxidation-derivative of the ethyl series—and propionic acid the oxidation-derivative of the propyl series. The oxidation of propione, an isomer of valeral ($C_8H_{10}O$), gives no acid higher in the scale than propionic acid.

2. On the Oxidation of Ethylamine.

By J. A. WANKLYN and ERNEST T. CHAPMAN.

WHEN ethylamine or sulphate of ethylamine is treated with bichromate of potash and sulphuric acid, little or no action takes place in the cold, even on long standing. On boiling, however, the ethylamine is attacked, though only slowly. As the solution becomes more concentrated, the reaction becomes brisker, and towards the end of the operation much gas is evolved. When the liquid has almost all distilled off, a reaction like that which takes place with ammonia and chromic acid occurs. Sulphate of ethylamine was boiled with bichromate of potash and dilute sulphuric acid. The vapours evolved passed first through a Liebig's condenser, and then into a receiver kept cool by ice and salt. The distillate was heated till a small quantity had distilled over. It smelt like aldehyde, and with it we obtained the ordinary reactions of that substance, *viz.*, formation of the silver mirror, and of the ammonia-compound.

The liquid which remained in the retort presented all the

characteristics of acetic acid. It was converted into a baryta-salt, and the per centage of barium determined.

·6306 grm. gave ·5738 Ba_2SO_4 or 53·5 per cent. Ba 53·7.

These numbers can leave no doubt that the substance in hand is acetic acid. A portion of the distillate which was supposed to contain aldehyde was heated in a sealed tube with a fresh portion of bichromate of potash and dilute sulphuric acid whereby it also was converted into acetic acid.

No ammonia could be detected in the mixture of chromate and sulphuric acid, even though examined before the violent final reaction. The method of examination adopted consisted in rendering a portion of the fluid from the retort, alkaline with potash, and then distilling into water; the solution so obtained was then neutralized with sulphuric acid and evaporated almost to dryness, and strong alcohol was added; this dissolves the sulphate of ethylamine, but not the sulphate of ammonia. This method of examination would not discover very small traces of ammonia, but would have detected any considerable quantity.

From the above it appears, therefore, that ethylamine yields by oxidation nitrogen, water, acetic acid and aldehyde.

3. *Action of Acids on Naphthylamine.* (Preliminary Notice.)

By ERNEST T. CHAPMAN.

IN a former paper, I mentioned several methods by which azodinaphthyldiamine may be produced.* These were;

First. Action of nascent hydrogen on dinitronaphthylin. (This method, however, I could not succeed in verifying.)

Second. Action of one equivalent of nitrous acid on two equivalents of naphthylamine. Both this and the preceding method were announced by Messrs. Perkin and Church.

Third. Action of nascent hydrogen on a mixture of nitro- and dinitronaphthalene.

Fourth. Action of zinc-ethyl on a similar mixture.

Fifth. Action of ammonia on a strongly acid solution containing naphthylamine and nitrous acid; it is to be remembered

* Chem. Soc. J. [2], iv, 135.

that potash cannot be substituted for ammonia in this preparation.

To these methods I may also add that a mixture of dry nitrite of potash and hydrochlorate of naphthylamine, if gently warmed, yields azodinaphthyl-diamine without difficulty, and only contaminated with chloride of potassium and the excess of nitrite employed.

I have now to announce an altogether new and very interesting method of obtaining this compound—one which, I think, is calculated to throw a new light on the atomic constitution of naphthylamine.

I observed, when previously working on these compounds, that naphthylamine is soluble in concentrated sulphuric acid, but that, on diluting this solution, I could not succeed in making it crystallise. As it is a well known fact that naphthylamine-salts frequently assume a colloid form, I did not investigate the causes of this phenomenon. Some observations, which I subsequently made, led me to examine this solution more carefully. I dissolved naphthylamine in cold concentrated sulphuric acid, and allowed it to stand over night. On examining it next morning, I found that it was perfectly colourless, and on diluting it with water and adding potash, a red precipitate was produced, instead of the white one, which might have been expected. This red precipitate, on the addition of acids, assumed a violet colour and was in short, azodinaphthyl-diamine. I naturally suspected oxides of nitrogen to be present in the sulphuric acid employed. This, however, was not the case. I then warmed some of the original solution. It became brilliantly green, the upper surface of the fluid being violet. On being poured into water, it did not immediately mix with it, and when it did mix, it turned violet. The violet colouring matter gradually separated out and was filtered off. It presented all the characters of a salt of azodinaphthyl-diamine. These characters are, insolubility in water, solubility in alcohol, the solution being a most magnificent violet, which is changed to an orange on the addition of an alkali; the original colour is re-obtained by the addition of an acid: if the acid be added drop by drop, the colour passes through various shades of red, crimson, and lilac before it re-assumes the original violet colour. It dissolves in concentrated sulphuric acid with a very beautiful blue colour. From this solution it is precipitated unaltered on the addition of water.

As many persons might consider the reactions of azodinaphthyl-diamine insufficient to establish its identity with the substance described in this paper, I have, with great labour, succeeded in obtaining a well crystallised sample, and determined the percentage of nitrogen it contained. It yielded the following numbers:—

·6405 of the base gave 77·5 c. c. N. (moist). Bar 755. Temp. 14° C.

∴ 75·4 c. c. at 760 bar. and 0° C.

∴ % of N. in substance 14·75.

Theory 14·14.

The preceding observations naturally led to a general examination of the action of acids on naphthylamine. The acids employed were the following:—Nordhausen sulphuric acid, and common sulphuric acid, phosphoric acid (obtained from the residue in the preparation of iodide of ethyl, and, therefore, free from all suspicion of oxides of nitrogen), oxalic, acetic, tartaric, citric, nitric, hydriodic, and hydrochloric acids. All these acids, with the exception of hydrochloric acid, when boiled with water and naphthylamine, produce colourless or but slightly coloured compounds, which, by the action of potash, yield azodinaphthyl-diamine. The nitric acid must, of course, be used dilute. The other acids appear to act best when concentrated, and indeed the largest yield is obtained by fusing together naphthylamine and oxalic acid. The resulting compound must be dissolved in boiling water, and precipitated with potash, carbonate of potash, or in some cases ammonia*. Curiously enough, I could not make hydrochloric acid produce this conversion of naphthylamine into azodinaphthyl-diamine. On a consideration of this reaction, it is evident that at least three equivalents of naphthylamine must be concerned in the formation of one of azodinaphthyl-diamine, and that there must also be secondary products formed. Of course the simplest view of the case is that three equivalents of naphthylamine coalesce, and that $C_{10}H_{12}$ is in some manner eliminated from them by the action of the acid. I have not yet succeeded in isolating the secondary product.

* Ammonia will answer in the case of sulphuric acid, but gives a colourless solution with the oxalic acid. I have not tried its action with any of the other acids.

Aniline (crude) apparently behaves in a similar manner, though I have not examined its action with any acid excepting sulphuric acid. If naphthylamine be boiled with dilute sulphuric acid, the resulting colourless solution need not be treated with an alkali or an alkaline carbonate; acetate or oxalate of potash produces the same effect, though of course the acetate or oxalate of the base is obtained instead of the base itself.

Sometimes the colourless solution obtained by boiling the naphthylamine with excess of acid yields only traces of the base on the addition of an alkali; nevertheless, the base itself may easily be obtained from such a solution by re-acidifying and re-precipitating.

When naphthylamine is heated with excess of hydrochloric acid, it yields, as usual, a colourless solution, which yields a red base by the addition of an alkali. This base, however, is not turned violet by the addition of an acid, but again becomes colourless. The only body, known to me, derived from naphthylamine having this peculiarity is ninaphthylamine. I have not examined the body, and cannot, therefore, do more than suggest the possibility of this red base being ninaphthylamine. I have worked with ninaphthylamine, and the substances present precisely similar appearances.

It has often been remarked, on attempting to recrystallise salts of naphthylamine, that they are apt to lose their power of crystallisation, and to become gummy. It is also well known that solutions of these salts cannot be kept without undergoing a similar change. On examining the mother-liquor from which the sulphate had been crystallised, I found that it yielded azodinaphthyldiamine by the action of alkalies.

Every one who has ever worked with naphthylamine must have observed that filter-papers, cloths, and, in fact, everything which comes much in contact with the solutions, assumes a reddish or violet colour, and I have observed that such papers may be turned orange by the action of an alkali, and regain their violet colour when acted upon by acids. It would appear, therefore, that this coloration is due to azodinaphthyldiamine.

4. *Production of Acetic and Propionic Acids from Amylic Alcohol.*

By ERNEST T. CHAPMAN.

THE starting point of the following investigation was nitrite of amyl. This substance was prepared from the alcohol by the action of nitrous acid in the usual manner. It was found to boil constantly at 98°C ., with the barometer at 750 mm.

The nitrite having been very carefully dried, was treated with anhydrous phosphoric acid. A violent reaction at once took place. The mixture became very hot—so hot that in one instance it took fire. The reaction may, however, be rendered quite manageable by cooling the vessel with water, and adding the nitrite little by little. Care should be taken *not* to add excess of nitrite. The reaction is not accompanied by disengagement of gas. The product is a brown solid mass.

A portion of it was heated with strong solution of potash. The distillate had a mouldy, ammoniacal smell, and strong alkaline reaction. It was rendered slightly acid with hydrochloric acid, evaporated almost to dryness, and bichloride of platinum was added in excess. A precipitate was soon formed. It was washed, dried, and the percentage of platinum determined. It corresponded with ammonio-bichloride of platinum.

The filtrate was then rendered slightly alkaline with potash when the mouldy smell was again produced; it has considerable resemblance to patchouli. On rendering the fluid strongly alkaline and heating, the smell of ammonia was again perceived. The mixture was then distilled, the distillate mixed with excess of strong potash, and heated in a sealed tube for about an hour at 120°C .

When the tube was opened, gas escaped, and there was a strong smell of ammonia, but the mouldy smell had disappeared. The contents of the tube were rendered acid with sulphuric acid, transferred to a small retort, and distilled. The distillate was free from sulphuric acid, but had a strongly acid reaction. It tasted and smelt like acetic acid. Another portion of the original substance was heated with caustic potash in such a manner that the fluid distilling off flowed back again on to the potash. Ammonia

was evolved, and the contents of the retort when distilled with sulphuric acid yielded a distillate free from sulphuric acid, but possessing a strongly acid reaction. It was neutralised with carbonate of baryta, boiled, and filtered. A measured volume of this solution was then evaporated to dryness, and the percentage of barium determined.

·2851 grm. salt gave ·2484 grm. Ba_2SO_4 ,
or 50·9 per cent.

This number is intermediate between 48·34, the percentage of propionate, and 53·72, the percentage of acetate.

Enough sulphuric acid was added to neutralise one-third of the baryta in another measured volume of this liquid, and the liquid was distilled. The distillate was then neutralised with carbonate of baryta, evaporated to dryness, and the percentage of barium determined.

·4675 grm. of the salt gave ·3848 Ba_2SO_4 .
∴ 48·45 % Ba. Theory 48·34.

As will be seen from the results, the numbers correspond with those required by the propionate. To the liquid in the retort as much more sulphuric acid was added, and the acid thereby liberated boiled off. As this liquid was sure to contain a mixture of the two acids, it was not further examined.

More sulphuric acid was then added, the distillate thus obtained was neutralised with carbonate of baryta, boiled, and filtered, the liquid was evaporated to dryness, and the percentage of barium determined.

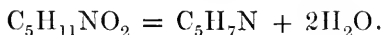
·5482 grm. salt gave ·5000 grm.
∴ 53·68 % Ba. Theory 53·72.

This number corresponds with that required by acetate of baryta.

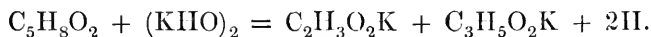
I have not been able to obtain the compound which has the mouldy smell free from ammonia, nor do I see how I could do so, as, when it is liberated from its compounds with acids by the action of potash, it always breaks up into ammonia and acids. A portion of the original substance was heated gently with strong potash-solution, and the liquid rendered acid by hydrochloric

acid. Under these circumstances, an acid with a most remarkable odour separates out, but I have not succeeded in obtaining any of its salts. When I attempted to recrystallise any of these compounds they underwent decomposition, and as I had not much of the substance, I abandoned the attempt. The nature of the above-mentioned reactions seems to be as follows:—

First. $C_5H_{11}NO_2$, by the action of P_2O_5 , is deprived of 2 eqs. of water, and is converted into C_5H_7N .



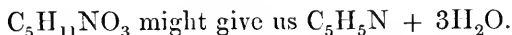
C_5H_7N may be regarded as the cyanide of an alcohol-radical of the allyl series (C_4H_7Cy). This, when acted upon by potash, should give ammonia and an acid isomeric or identical with angelic acid. Now, angelic acid, as is well known, splits up when heated with potash, yielding acetic and propionic acids:



The most remarkable thing about this reaction is the ease with which it takes place, even at comparatively very moderate temperatures.

The question naturally suggests itself what would be the action of anhydrous phosphoric acid on other members of the same class of ethers. What, for instance, would happen if the nitrite of ethyl were treated in the same way? Should we obtain 2 eqs. of formic acid as the last product? And what could we obtain from nitrite of methyl?

Phosphoric acid attacks nitrates as well as nitrites, though not so easily, and this may prove to be a method of obtaining compounds of the same class as picoline.



There is one aspect of the subject which deserves attention. In the reactions above described, we have seen that ordinary amyl alcohol splits up into the groups C_3 and C_2 . Why does it not split up into the groups C_4 and C ? Possibly ordinary amyl alcohol is not strictly a primary alcohol.

5. *On some Decompositions of Nitrite of Amyl.*

By ERNEST T. CHAPMAN.

1st. *Action of Oxidizing Agents :—*

Nitrite of amyl was treated with bichromate of potash and sulphuric acid. The operation was conducted in a retort with a condenser so arranged that the condensed vapours ran back into the retort. Bichromate of potash and dilute sulphuric acid were introduced into the retort and raised to the boiling point. The nitrite was then added drop by drop from a stop-cock dropping funnel. The reaction is very brisk, but no permanent gas is evolved. As soon as the reaction was finished, about a third of the contents of the retort were distilled over. The distillate consisted of two layers, and had a smell resembling that of pine apples; it was agitated with carbonate of soda. Brisk effervescence ensued and a considerable portion of the oily layer disappeared, the remainder was decanted, dried over chloride of calcium (of which it dissolves a considerable quantity,) distilled off and fractionally distilled. It began to boil at 130° , but only a few drops passed over until the temperature had reached 185° , between which and 187° the whole of the liquid distilled over. A portion of the distillate was digested with caustic potash in aqueous solution. The product of this operation was put into a retort and about a third distilled over. The distillate consisted of two layers. It was saturated with sulphate of soda, which greatly increased the amount of the oily layer; this latter was then decanted, dried, and distilled. It presented all the characteristics of ordinary amylic alcohol, boiling point 132° . The liquid remaining in the retort was then rendered strongly acid with sulphuric acid, and a portion distilled over. This distillate also separated into two layers and presented the smell and characters of valerianic acid. A portion of the oily layer was dried and distilled; it boiled at 173° . The remainder of the distillate was boiled with excess of carbonate of baryta, filtered, evaporated to dryness, and the percentage of barium determined: it yielded the following numbers :—

Salt taken 4466
 \therefore Ba % 40.32

Ba_2SO_4 found 3062
 Theory 40.42

The aqueous portion of the original distillate was boiled, with a view of expelling any of the oily matters that might have remained in solution. To a portion of it, iodide of potassium, acetic acid, and starch-paste were added: no blue coloration was produced, whence the absence of nitrites may be inferred. Another portion of this liquid was then tested for nitrates with proto-salt of iron and sulphuric acid; nitric acid was present in abundance. The liquid was now saturated with sulphate of soda, and dilute sulphuric acid added; an oily layer at once rose to the surface. It was decanted, dried, and distilled, it also boiled at 173° , and smelt like valerianic acid. It was converted into a baryta-salt and the percentage of barium determined. It gave the following numbers:—

Salt taken 3938
 \therefore Ba % 40.32

Ba_2SO_4 found 2700
 Theory 40.42

From the above it appears that nitrite of amyl is converted by the oxidizing action of chromic acid into nitric acid, valerianic acid, and valerianate of amyl.

2nd. *Action of Sulphuric acid on Nitrite of Amyl.*

Concentrated sulphuric acid attacks nitrite of amyl with great energy, red fumes are evolved in abundance, and occasionally the liquid catches fire. The product is a black, foul-smelling liquid. As charring evidently takes place, it was not further examined. I then made some experiments to determine how dilute an acid could be employed to effect this decomposition, and, after many trials, came to the conclusion that the best acid to employ was a mixture of two volumes of water and one of concentrated sulphuric acid. This liquid has little or no action on the nitrite in the cold, but at a few degrees above 100°C . it attacks it pretty readily. The apparatus employed in this experiment was similar to that already described, with the exception that arrangements were made to collect and examine the gas evolved.

Great care is required in this experiment, as, if the temperature rises too high, charring occurs, and of course the result is complicated by secondary products; if the temperature is not sufficiently high, the decomposition proceeds irregularly, and the evolution of gas takes place in bursts. The nitrite of amyl was added drop by drop, and the temperature so regulated as to keep up a gentle and continuous evolution of gas.

Examination of the gas:—The gas when collected over mercury

or water is perfectly colourless; if collected over mercury, or if examined immediately after being collected over water, it appears to be inflammable, this, however, is due to vapours suspended in the gas; for on agitation with water, this property disappears. If a stream of the gas be directed into a damp flask, the flask is immediately filled with red fumes, and a white crystalline substance is deposited. On dissolving this in water, and adding chloride of barium and hydrochloric acid, an abundant precipitate is at once obtained. The gas is completely soluble in solution of protochloride of iron. It contains no carbonic acid, as was conclusively proved by the following experiment. A Liebig's potash apparatus was charged with a mixture of bichromate of potash, chloride of barium, and dilute hydrochloric acid. When the gas was passed slowly through this and then into lime water, not the slightest turbidity was produced, though sulphate of baryta was precipitated in the potash bulbs; it appears, therefore, that the gas is a mixture of sulphurous acid and nitric oxide; and further that no other gas is present.

Examination of the liquid products. As soon as the smell of nitrite of amyl had disappeared, water was added and about one-third of the contents of the retort was distilled off and treated precisely in the same manner as that described in the former section (action of oxidizing agents). It yielded, first, a neutral oily liquid boiling at the same temperature as the valerianate of amyl mentioned in the previous experiment (186°C.), and having the same odour. By treatment with potash it yielded a liquid having the characteristics of amylic alcohol, and also an acid having the smell and saturating capacity of valerianic acid, as shown by the following determination of the percentage of barium in its baryta salt:—

Salt taken $\cdot 3088$

\therefore Ba % $40\cdot 44$

BaSO_4 found $\cdot 2124$

Theory $40\cdot 42$

2nd. A very small quantity of valerianic acid was dissolved out of the original distillate by carbonate of soda. Converted into a baryta salt it yielded the following numbers:—

Salt taken $\cdot 2916$

\therefore Ba % $40\cdot 39$

BaSO_4 found $\cdot 2004$

I find, therefore, that nitrite of amyl and sulphuric acid react upon each other, producing sulphurous acid, water, and valeria-

nate of amyl. The trace of valerianic acid formed is doubtless due to a secondary reaction. The following equation would show the change :—



3rd. *Action of Hydriodic acid on Nitrite of Amyl.*

Concentrated hydriodic acid acts upon nitrite of amyl in the cold, very little rise of temperature taking place, although iodine is liberated abundantly.

Concentrated hydriodic acid and phosphorus were introduced into the apparatus already described, gently warmed, and nitrite of amyl added drop by drop. A colourless gas is evolved in abundance, which produces dense red fumes on coming in contact with the air; it is completely soluble in protochloride of iron, and is, in fact, nitric oxide.

On distilling the contents of the retort, a heavy oily liquid passes over. It was washed with dilute solution of carbonate of soda, dried over chloride of calcium, and distilled. It boiled constantly at 146°C . A weighed quantity of it was digested with alcoholic potash, and the amount of iodine determined; $\cdot 3624$ of the substance gave $\cdot 4276$ of iodide of silver.

$$\therefore 63\cdot 76 \% \text{ I} \qquad \text{theory} \qquad 64\cdot 13 \% \text{ I}$$

These numbers can leave no doubt that the substance in hand is iodide of amyl.

Permanganate of potash also oxidizes nitrite of amyl. I have not fully investigated the products, but they appear to be the same as those obtained by the action of chromic acid.

XXXI.—*Preliminary Notice on Phthalic Aldehyde.*

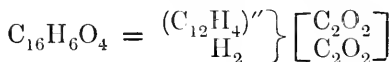
By H. KOLBE and G. WIRCHIN.

A SHORT time ago* one of us predicted the existence of a hitherto unknown class of chemical compounds, namely, the aldehydes and alcohols of polybasic acids. We have since made numerous experiments with the view of discovering some of the members of

* Chem. Soc. J. [2], iv, 54 (Feb, 1866).

this group, and believe that we have succeeded in preparing phthalic aldehyde.

Phthalic chloride, treated with zinc and hydrochloric acid, is converted into a brownish-yellow unctuous mass, which, after dilution with a large quantity of water, may be extracted with ether; and if the residue left on evaporating the ethereal solution be shaken up with a small quantity of aqueous carbonate of ammonia, to remove any phthalic acid that may be present, the insoluble residue again dissolved in ether after repeated agitation with water, and the clear ethereal filtrate evaporated, after treatment with animal charcoal, there remains a compound having exactly the composition of phthalic aldehyde,



Phthalic aldehyde is a white, crystalline, easily fusible substance having a faint aromatic odour. It melts at 65°C ., dissolves easily in alcohol and ether, very sparingly in cold water, more freely in boiling water, and crystallises from the latter solution by slow cooling in small rhombic plates. When carefully heated in small quantities, it sublimes apparently undecomposed; but larger quantities, when heated, turn brown, and suffer partial decomposition.

On mixing the warm aqueous solution with a concentrated solution of acid sulphite of sodium, the liquid solidifies, after a while, to a mass of long, slender, silky needles, probably a compound of sulphurous acid with soda and phthalic aldehyde.

A mixture of potassic chromate and sulphuric acid exerts but little oxidising action on phthalic aldehyde.

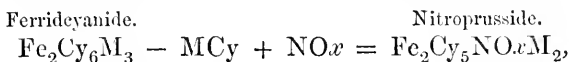
Phthalic acid, treated in a slightly acid solution with sodium-amalgam, undergoes a similar transformation. By prolonged action there is formed, besides the aldehyde, another body, probably the alcohol of phthalic acid.

We are continuing the investigation, and extending it to other polybasic acids.

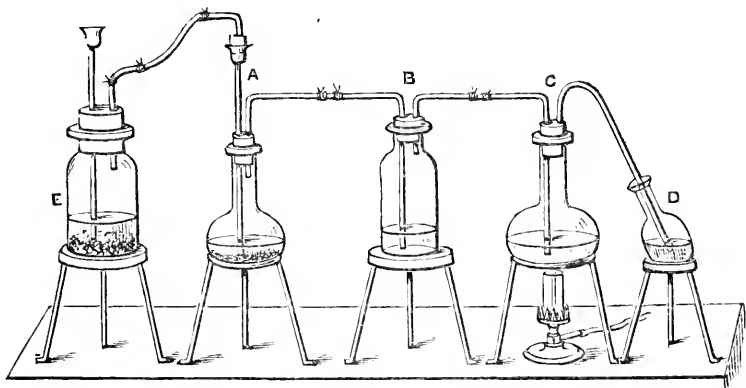
XXXII.—*The Nitroprussides.*

By EDWARD ASH HADOW, King's College.

THE nitroprussides have allured me for years by the beauty of their reaction with soluble sulphides, and also because there is an evident uncertainty about their composition. They are evidently formed on the type of the ferridecyanides. Thus:



The only doubtful question seems to be *what* oxide of nitrogen replaces the MCy. A mere glance at Playfair's most laborious and careful ultimate analyses showed the hopelessness of endeavouring to gain light in this way by improving on them. The only conclusive proof, it was felt, would be the actual formation of nitroprusside from ferridecyanide by the displacement of an atom of alkaline cyanide by one of the oxides of nitrogen. Protoxide of nitrogen, NO, being generally rejected in published formulæ, was not tried; but as Gerhardt and almost all other chemists represent it as the binoxide NO₂, an apparatus was fitted up as follows, for the purpose of testing the correctness of this view:—



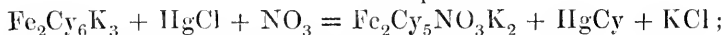
The flask C has a solution of pure ferridecyanide acidulated with sulphuric acid and kept hot, so that the binoxide NO₂, instead of having to displace MCy, has the far easier work of displacing HCy, if it can. The whole apparatus was first filled with car-

bonic acid to expel oxygen, and pure nitric oxide (NO_2) from A, washed from any nitrous acid in B, was then passed in for some time. Flask C by degrees became very blue and muddy, and when, after an hour, the contents were examined, *no trace* of nitroprusside was found.

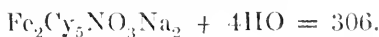
The operation was then exactly repeated, only that instead of pure nitric oxide the red nitrous acid vapours from starch and nitric acid were passed in. The difference was wonderful; *no* Prussian blue appeared in flask C. The colour changed rapidly to the red of nitroprusside, and much hydrocyanic acid came off into D; and on opening the flask all ferridecyanide of potassium had disappeared, the conversion to nitroprusside being almost perfect. Since then I have never had a doubt but that the generally received formula $\text{Fe}_2\text{Cy}_5\text{NO}_2\text{Na}_2$ was wrong, and that the true formula has NO_3 or NO_4 instead, but which, the last experiment does not determine, for NO_3 from starch always has NO_4 mixed with it. The presence of NO_3 or NO_4 as the nitrogen-oxygen essential to nitroprusside, is further shown by a very simple experiment—the reverse of the last. On adding to a solution of pure nitroprusside a solution of potash and some prussic acid, and warming, the red of the nitroprusside changes for an instant to deep yellow, and then to pale yellow. The solution will be found to contain ferridecyanide, with plenty of nitrite, but no trace of nitroprusside. Here NO_3 or NO_4 has been displaced by KC_y , and ferridecyanide reproduced.

I felt that nothing could be conclusive but the actual displacement of an alkaline cyanide in ferridecyanide by pure NO_3 , which can be obtained by the action of acetic acid on an alkaline nitrite, which mixture absolutely excludes NO_4 . After trying many methods for displacing KC_y in ferridecyanide of potassium, the following experiment was tried with perfect success:—Ferridecyanide of potassium solution was mixed with a solution of corrosive sublimate and acetic acid, and a nitrite added, and the whole was left for some hours, when, on examining the mixture, nitroprusside was found in abundance, which experiment conclusively stamped NO_3 as the oxide. The reaction was as follows:—

Nitroprusside.



and the true formula of the sodium-salt is



The fact of this being the true formula is further confirmed by the close correspondence between the percentage of each of the elements calculated from this formula and Playfair's own numbers, which is closer than the numbers derived from Gerhardt's formula.

	Calc. from NO_3 formula.	Playfair's.	Gerhardt's NO_2 formula.
C	= 19.6	19.5	20.1
N	= 27.5	27.8	28.1
Fe	= 18.3	19.3	18.8
Na	= 15.0	15.2	15.4
H	= 1.3	1.3	1.3
O	= 18.3	—	16.3
	<hr/> 100.0		<hr/> 100.0

The success of this reaction on the small scale suggested it as a means of manufacturing nitroprusside on the large scale. The present retail price of the sodium-salt, 6s. per oz., or £4 16s. per lb., while the ferrocyanide from which it is derived is worth about 1s. 6d. per lb., sufficiently shows the difficulties attending the present method.

After very many experiments the following method has been arrived at, which, though by no means perfect, will furnish nitroprusside of sodium by the pound without difficulty.

1. A strong solution of caustic soda is prepared, and thoroughly saturated with the nitrous acid vapours from starch and nitric acid (old battery acid does well). The amount of true nitrite of soda, NaONO_2 , in this solution is determined by permanganate by taking a small measured quantity, diluting largely with water, acidifying with sulphuric acid, and observing the amount of standard permanganate decolorised. $\text{Fe}_4 = \text{NaO} \cdot \text{NO}_2$ in decolorising power. The amount of real nitrite of soda in the solution being known, is recorded on the bottle.

A mixture of any bulk is then made in the following proportions:—

A	{ Ferrideyanide of potassium 332 grs. Acetic acid (Beaufoy's) .. 800 grs.	} in $\frac{1}{2}$ pint of boiling water,
B	{ Corrosive sublimate .. 164 grs. Solution of nitrite soda = 80 grs. of true NaONO_2	} make up to $\frac{1}{2}$ pint with cold water,

adding acetic acid, if necessary, until quite clear. Pour the cold solution B into the hot solution A. The mixture becomes at

first turbid, but in a few minutes afterwards quite transparent. It should be kept at a temperature of 140° (at which point little nitrous acid is lost) for some hours, with addition, if necessary, of more nitrite of soda and acetic acid from time to time, until all ferridecyanide has disappeared. When this is the case, the whole mixture may be boiled down, until, on cooling, it solidifies to a thick paste. The right state of concentration has been attained, when on beating the paste up, and squeezing in linen, a *pale* syrup, chiefly of acetate of potash, is expressed. The pearly-looking mass freed from acetate of potash, as far as possible, must be redissolved in such an amount of boiling water, that on cooling a large proportion of cyanide of mercury separates in white pearly scales, quite free from nitroprusside crystals. On squeezing in linen, a deep-red solution of nitroprusside is expressed, and a white, pearly mass of cyanide of mercury remains on the linen. On concentrating the red filtrate, a large crop of crystals of nitroprusside of sodium is obtained in a mother-liquid containing more or less cyanide of mercury, in pearly scales, easily separated by throwing the whole on a moderately coarse hair sieve, which will retain the prisms of nitroprussides of sodium, and allow the cyanide of mercury to pass through. The prisms may be washed quite clean by allowing the cyanide of mercury to settle down in the filtrate, and using the clear supernatant fluid for washing. The operation can, of course, be continued as far as it may be deemed profitable. If the cyanide of mercury is not wanted as such, it can be made to furnish hydrocyanic acid and corrosive sublimate for use again, by boiling with hydrochloric acid.

It may be added, in conclusion, that nitroprussides react well only with monosulphides. The more of a persulphide the solution contains, and the deeper the yellow colour, the less distinct is the reaction. This difficulty can be overcome by warming the yellow persulphide with sufficient cyanide of potassium to decolorise it, when the beautiful carmine of the monosulphide will be obtained.

XXXIII.—*The Platinum-bases: the best mode of obtaining and identifying them; some new Compounds.*

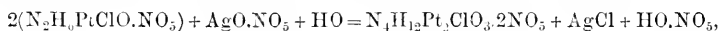
By EDWARD ASH HADOW, King's College.

ON first attempting to prepare the platinum-bases as specimens for Dr. Miller's lecture table, I encountered various perplexing difficulties, arising from the endless number of compounds that could be formed, and I felt the want of ready methods for recognising the class to which any unknown salt belonged, whether platosamine or diplatosamine, platinamine, or diplatinamine, or chlorodiplatinamine, as Gros' or Raewsky's salts. The source, too, of all these salts is always the green salt of Magnus, the preparation of which, in any quantity, is attended with the greatest uncertainty, and if too much sulphurous acid has been used to reduce the bichloride of platinum, is often a total failure. Then again, when it is obtained and used for forming Gros' and Raewsky's nitrate, half the platinum is wasted as chloride or nitrate. Disheartened by such a mode of proceeding, I determined to proceed by an entirely different method, and to convert a certain weight of metallic platinum into its equivalent of pure dry protochloride by heat in the usual manner. When the protochloride thus obtained is digested in warm, moderately strong ammonia, it dissolves gradually but completely, excepting a little iridium and oxide of iron, giving a brownish solution. On filtering and concentrating, a large crop of fine prisms of hydrochlorate of diplatosamine is obtained, which is the source of all the other bases. These crystals contain an atom of water, $N_2H_6PtCl \cdot H_2O$, which is not usually given in books, and which, to my cost, I did not discover for some time, and graduating my permanganate solutions by the salt as if anhydrous, I met with most perplexing results.

Gros' nitrate ($N_2H_6PtClO \cdot NO_5$) is obtained from this salt by pouring a hot solution of it into hot, moderately concentrated nitric acid; abundance of red fumes are evolved, and a thick paste of small crystals of Gros' nitrate forms at the bottom of the acid, in which it is almost insoluble; it can be drained on asbestos, and dried at about 280° Fahr.; when re-crystallised from water it gives brilliant flat prisms.

Raewsky's nitrate is obtained easily and abundantly from

Gros' salt by boiling the latter for some hours with nitrate of silver and some nitric acid; but no excess of nitrate of silver can remove the chlorine from Raewsky's nitrate, and reduce it to a nitrate of diplatinamine, from which it differs totally in all its properties; analysis completely confirms the correctness of Gerhardt's formula for Raewsky's nitrate, $N_4H_{12}Pt_2ClO_3 \cdot 2NO_5$, $HO = 442$.—Raewsky's own formula, $N_4H_{12}Pt_2ClO_5 \cdot 2NO_5$ is obviously impossible, Pt_2 being brought to the platinic state by $Cl + O_3$, leaving O_2 in excess. The above being the formula for Raewsky's nitrate, its derivation from Gros' nitrate by nitrate of silver is simple enough; 2 atoms of Gros' nitrate unite, and losing an atom of chlorine, gain one of oxygen—



so that 2 atoms of Gros' nitrate, or 462 parts, require 1 atom of nitrate of silver for the decomposition; but in practice it is better to use rather more, or about 190 parts of the nitrate of silver. After filtering from chloride of silver, it is well to boil the solution again, to make sure that the transformation is complete. After the decomposition has ceased, the filtered solution is somewhat concentrated by evaporation and allowed to cool, when Raewsky's nitrate crystallises abundantly; it can be treated as Gros' salt, washing away the solution of nitrate of silver with diluted nitric acid, and drying at $280^\circ F$.

From the singular proportion that exists between the acid and the oxygen in Raewsky's nitrate, I had the curiosity to ascertain what the composition of the hydrochlorate would be, and therefore added chloride of ammonium in excess to Raewsky's nitrate, collected the precipitate of minute prisms thus produced, and washed with alcohol till clean. The hydrochlorate was found to have the composition $N_4H_{12}Pt_2Cl_3O$.

With regard to discovering the class to which a base belongs, platamine and diplatamine salts correspond, in their reducing action on permanganate of potash, to the protochloride of platinum, from which they are derived. The diplatamine-salts are readily recognised by their property of yielding Magnus' green salt when treated with a solution of protochloride of platinum. Magnus' green is only one of a large series of double salts that hydrochlorate of diplatamine is capable of forming with other metallic chlorides, such as corrosive sublimate and the chlorides of cadmium, palladium, tin, and copper. The double salts formed

with cadmium and with mercury were analysed, and found to have the same composition—1 atom of each salt. The diplatosamine-salts are further characterised by the beautiful blue or green precipitate or solution, which they furnish when a current of nitrous acid is passed into their strongly acidified solution. None of these reactions are exhibited by the platosamine-salts, which possess little interest.

The diplatinamine, chlorodiplatinamine, and platinamine salts have, of course, no reducing action on solutions of the permanganates. The two series of most interest, viz., those of Gros and of Raewsky, are readily distinguished. Chloride of ammonium gives with the salts of Gros' series, an insoluble, and with those of Raewsky's, a soluble chloride; a single drop of solution of sulphate of soda with a drop of solution of Gros' nitrate, on stirring, gives hairy tufts, which are deposited on the lines of stirring, but no change occurs when Raewsky's nitrate is similarly treated. But the most characteristic reaction of Raewsky's nitrate is that of giving, with a very dilute solution of protochloride of platinum strongly acidulated with nitric acid, a beautiful, coppery, moss-like precipitate, exactly resembling in appearance the platinideyanide of potassium; Gros' nitrate has no such reaction.

The diplatinamine-salts are quite uninteresting; they give with chlorides, after some time, large crystals of the hydrochlorate; they may readily be recognised by being reduced by sulphurous acid to salts of diplatosamine, whereas platinamine-salts, by the same agent, are reduced to salts of platosamine.

The reaction between nitrous acid and acidulated salts of diplatosamine seems most singularly to have been overlooked. I have examined two of the compounds, one of which is blue and the other green. The blue compound is obtained with nitrate of diplatosamine (obtained from the hydrochlorate by double decomposition with nitrate of silver), by acidulating its solution strongly with nitric acid, and passing in nitrous acid vapours. A beautiful smalt-blue precipitate then falls in abundance, which, under the microscope, is seen to consist of dodecahedrons. The green precipitate is less beautiful, and is obtained by passing nitrous acid into hydrochlorate of diplatosamine strongly acidulated with hydrochloric acid. These precipitates can be drained on asbestos and afterwards washed with dilute hydrochloric and nitric acids respectively; they may be dried without visible change at 212° . Some very simple experiments served to show qualitatively the

composition of these precipitates. Placed in pure water, both precipitates soon dissolve, furnishing blue and green liquids respectively, smelling strongly of nitrous acid; on gently warming, the nitrous acid goes off, leaving unchanged diplatosamine-salts strongly acid with hydrochloric and nitric acids. If, instead of expelling the nitrous acid by heat, the corresponding acids be added to each solution, the original precipitate will be obtained unaltered. These precipitates appear, therefore, to consist, the blue of nitrate of diplatosamine with nitric and nitrous acids, and the green of the hydrochlorate of diplatosamine with hydrochloric and nitrous acids. The nitrous acid manifestly acts in these compounds the part of a base, nor is this the only instance in which it appears to do so. In the crystalline body of the leaden chambers, $\text{NO}_3 \cdot 2\text{SO}_3$, as well as in Frémy's sulphammonates, it appears to act a basic part; further, the analogy between SbO_3 and NO_3 would lead us to expect in the latter signs of a basic character. Peroxide of nitrogen has all the characters of a nitrate of the oxide NO_3 . It may be well to mention here that the instability of nitrous acid is in most chemical works greatly over-estimated, it being stated to be instantly decomposed by water. My own experience indicates quite the reverse, and if the water be acidulated, the nitrous acid appears to be remarkably stable.

These nitrous compounds were analysed by determining the amount of platinum in each, and then, by means of standard permanganate, determining the amount of oxygen capable of being absorbed. One atom of platinum (99), as diplatosamine, can only take up 1 atom (8) of oxygen. All absorbed beyond this is due to nitrous acid.

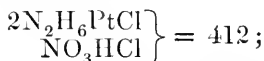
The blue nitrate dried at 212° gave 40·8 per cent. of platinum, and in one experiment it was found capable of absorbing 15·06 by weight of oxygen, for every one atom of platinum (99), evidently pointing to 16 parts, or 2 atoms, of oxygen; but as 1 atom of nitrous acid absorbs 2 atoms of oxygen, there can be only 1 atom of nitrous acid present to 2 atoms of platinum as diplatosamine: this points to the formula $\left\{ \begin{smallmatrix} 2(\text{N}_2\text{H}_6\text{PtO} \cdot \text{NO}_5) \\ \text{NO}_3 \cdot \text{NO}_5 \end{smallmatrix} \right\} = 482$, which is sufficiently confirmed by the following percentages:—

	Found.	Calculated from Formula.
Oxygen absorbable =	6·2	6·6
Platinum =	40·8	41·0

As a further confirmation, the percentage of nitrogen was determined volumetrically, and found to be 80.48 cubic inches per 100 grs. of blue nitrate. Reduced to weight it gives—

	Found.	Calculated.
Nitrogen	24.3	23.2

The green hydrochlorate appears under the microscope as feathery stars, not so readily soluble in water as the blue nitrate. The formula of the blue nitrate at once suggested that of the green hydrochlorate, namely :—



which was sufficiently confirmed by analysis.

	Found.	Calculated from Formula.
Platinum	= 48.8	47.94
Chlorine	= 26.07	26.15
Oxygen absorbable	= 7.51	7.74

It was a far more difficult task to determine the composition of the coppery precipitate given by Raewsky's nitrate with an acid solution of protochloride of platinum. Qualitative experiments tell much with regard to it.

The following facts are readily ascertained :—

1. Boiled in water, it is resolved into Magnus' green, Gros' nitrate, and protochloride of platinum—the two latter in equal number of atoms.

2. The proportion of platinum to chlorine is one atom of each, just as in the green compound of Magnus.

3. If a reducing agent such as sulphate of iron be added to the solution, instead of boiling the liquid, the quantity of Magnus' green is sensibly increased, owing to the reduction of Gros' nitrate to hydrochlorate of diplatamine, which, with the protochloride of platinum present, occasions the additional amount of the green precipitate.

4. These reactions plainly point to a formula of this kind $x(\text{N}_2\text{H}_6\text{Pt}_2\text{Cl}_2)\text{O}.\text{NO}_3$. The difficulty has been to find the value of x , and this has been due to the excessive uncertainty of the composition of the various samples of the coppery body, as is shown at once by ascertaining the percentage of platinum, which varies from 62 in the worst to 56 in the best looking product.

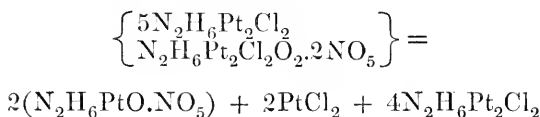
Then, again, it was found difficult to bring the salt into solution unchanged in composition for graduation by permanganate. This

appears to be best effected by digesting the compound in a solution of Raewsky's nitrate containing excess of dilute sulphuric acid. Determinations of the proportion of platinum in the platinic state have given numbers varying from 1 in 6 of total platinum in the best, to 1 in 10 in the worst. From these uncertain results I am only able to give a theoretical formula, being prevented from making any further experiments for some time to come; but of the correctness of the formula I feel pretty confident.

Theoretical composition of the coppery salt—

$$\left\{ \begin{array}{l} 5(\text{N}_2\text{H}_6\text{Pt}_2\text{Cl}_2) \\ \text{N}_2\text{H}_6\text{Pt}_2\text{Cl}_2\text{O}_2.2\text{NO}_5 \end{array} \right\} = 1940;$$

it is thus seen to have a similar composition to that of the platinid-cyanides* $\left\{ \begin{array}{l} 5(\text{KC}_y.\text{PtC}_y) \\ \text{KC}_y \text{ PtC}_y.\text{Cl} \end{array} \right\}$, $\frac{5}{6}$ of the platinum in each being in the platinous, and $\frac{1}{6}$ of each in the platinic state. The decomposition by boiling in water would be—

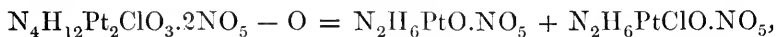


All the experiments alluded to were made with the coppery salt, prepared by mixing Raewsky's nitrate with a solution of protochloride of platinum highly acidified with nitric acid; a far better method, more easy, more profitable and more sure, has only lately been discovered. This consists in immersing the green compound of Magnus for some hours in a highly dilute solution of Raewsky's nitrate strongly acidified with nitric acid, and in large excess; the green salt then expands greatly in bulk and becomes brilliantly coppery. A brilliant sample of this salt gave 59.2 per cent. of platinum; the above formula requires 60.9. On boiling the product in water, the green compound of Magnus which was formed contained platinum equal to 40 per cent. of the weight of the salt, thus corresponding exactly with the decomposition which occurs when the copper-compound is simply boiled with water, in which case $\frac{4}{6}$ of the platinum separates as the green salt of Magnus.

In the formation of this coppery salt, by the above method,

* Chem. Soc. J. vol. xiii, 1861, p. 113.

a rather singular decomposition of Raewsky's nitrate occurs thus—



or by the loss of an atom of oxygen, which it imparts to the Magnus' green, it is reduced to equal numbers of atoms of Gros' nitrate and nitrate of diplatamine. Sulphate of soda will show the presence of the former, and nitrous acid that of the latter salt. The same reaction can be shown in another way. Raewsky's nitrate and sulphate of soda may be left mixed without change; but on adding a small quantity of a reducing agent, such as proto-sulphate of iron, the characteristic crystals of Gros' sulphate appear in a few minutes.

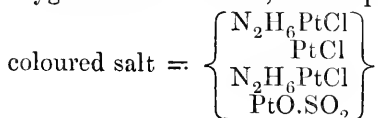
The singular composition of these coppery bodies seems to point towards the existence of an oxide of platinum having the composition Pt_6O_7 . I have not as yet obtained any proof of its existence, but I cannot help thinking it will one day be indicated by some characteristic of colour or form, &c., distinguishing it from the protoxide and peroxide.

There are one or two isolated facts which I may as well insert here by way of conclusion. On one occasion wishing to prepare the green salt of Magnus, protochloride of platinum was prepared with sulphurous acid as usual, the solution was divided into equal parts, and one-half was converted into hydrochlorate of diplatamine by ammonia and mixed with the other half, when, instead of the usual green, a dove-coloured precipitate fell; it was not altered by boiling, simply dissolving and crystallising out of the same colour. On determining the platinum, it corresponded perfectly with that in the green compound—

Green compound gave Pt = 64.3

Dove-coloured compound, Pt = 64.62.

On boiling in hydrochloric acid, however, it became quite green, and on testing with zinc and hydrochloric acid, sulphuretted hydrogen came off directly, proving the presence of sulphurous acid. To determine the amount of sulphurous acid, the dove-coloured salt was dissolved in ammonia and graduated by permanganate. It was found that for every 2 atoms of platinum, $2\frac{1}{2}$ atoms of oxygen were absorbed, which points to a formula for the dove-



I must also here remark that since writing this paper, I have looked into Graham's Chemistry on nitrous acid, and I was not a little gratified to find that he ascribes to nitrous acid a thoroughly basic character, a view I had not noticed in his or other works.

XXXIV.—*On a Cyanogen-derivative of Marsh-gas.*

By HENRY BASSETT.

THE action of cyanide of potassium on chloropicrin appeared, from the other reactions of the latter substance, to promise interesting results. The experiments made in this direction have led to the production of a substance representing chloropicrin in which 2 atoms of chlorine are replaced by cyanogen.

The process adopted was as follows:—

15 grms. of the best fused cyanide of potassium are dissolved in $1\frac{1}{2}$ oz. water, $\frac{3}{4}$ oz. alcohol added, and then 10 grms. chloropicrin.

The flask containing the mixture is fitted with a long condensing tube, and then placed on a water-bath till the reaction is started. It must then be quickly removed, and the upper end of the tube inserted into an opening in the chimney, to avoid inconvenience from the pungent vapours. The liquid rapidly becomes dark red, and a very violent reaction takes place for about ten minutes, sometimes necessitating the cooling of the flask towards the end of that time. The quantities mentioned cannot be safely exceeded, and the proportion of alcohol must not be sufficient to dissolve the chloropicrin, as the action then becomes almost explosive.

The contents of a sufficient number of flasks, when cold, are agitated with ether, and the resulting dark red ethereal solution is separated. The watery liquid remaining is dark brown, from the presence of a considerable quantity of the substances known as azulmic or paracyanic acids, and contains chloride, nitrite, carbonate, and oxalate of potassium, and large quantities of ammonia.

The ethereal solution is heated in a retort in the water-bath, to separate the ether and alcohol as far as possible, and the heat should not be continued too long, the substance being thereby

altered. The residue is mixed with water and filtered from some insoluble matter, the filtrate saturated with chloride of sodium, agitated with ether, separated, and the ethereal solution evaporated in an open vessel at very gentle heat.

The substance thus obtained is semi-fluid, of a dark red colour, does not solidify at -20° , has a peculiar and unpleasant smell, and is soluble in all proportions in water, alcohol, ether, chloroform, &c., the solutions staining the skin bright yellow.

It retains a considerable quantity of water, which is not given up over sulphuric acid in vacuo; neither can it be dried by heat, as even at ordinary temperatures it slowly alters, and near 100° it is completely decomposed. In the solution obtained by boiling it with potash, the presence of chloride, nitrite, and cyanide is readily detected by the usual tests, and large quantities of ammonia are formed.

It was obviously useless to attempt the analysis of this substance, but I think its composition is sufficiently indicated by the analyses of its compounds with oxide of lead and nitrate of silver.

The watery solution was mixed with excess of acetate of lead, filtered from any slight precipitate, and ammonia cautiously added, taking care not to use sufficient to render the liquid alkaline; the bright orange precipitate washed with boiling water and dried at 100° , bears a high temperature without decomposition, and is extremely hygroscopic.

I. .32 gram. gave .3615 gram. $\text{Pb}''\text{SO}_4$.

II. 1.01 gram. gave .18 gram. AgCl (dissolved in cold dilute nitric acid, nitrate of silver added, and then heated with excess of strong nitric acid till completely decomposed).

III. 3.084 grms. gave .509 gram. CO_2 and .07 gram. H_2O .

IV. .3195 gram. (another preparation) gave .3585 gram. $\text{Pb}''\text{SO}_4$.

V. .994 gram. gave .184 gram. AgCl .

VI. 1.113 gram. gave 28.3 c. c. N. at 0° and 760 mm.

These results lead to the formula $\text{CNO}_2\text{ClC}_Y_2 + 3\text{Pb}''\text{O}$.

	I.	II.	Theory.
Lead	77.19	76.65	76.24
Chlorine	4.41	4.58	4.35
Carbon	4.50	—	4.42
Hydrogen ..	.25	—	—
Nitrogen. . . .	—	3.19	5.16

The percentage of nitrogen is too low, but the fact that the other constituents are all rather in excess of the amounts required, and the impossibility of purifying the substance, will, I think, account for this.

The silver-compound is precipitated as a bulky orange-coloured powder on adding nitrate of silver to the solution of the original substance. It must be washed with cold water, in which it is slightly soluble, and dried *in vacuo*.

I. .7287 grm. heated with strong nitric acid till completely decomposed, gave .248 grm. AgCl, or 8.42 p. c. chlorine.

II. Filtrate from the above, mixed with hydrochloric acid, gave .0835 grm. AgCl, which, added to the former quantity, gives .3315 grm. AgCl to represent the whole amount of silver in the substance, or 34.24 p. c.

III. .4615 grm. decomposed with hydrochloric acid gave .209 grm. AgCl, or 34.08 p. c. silver.

The formula $3\text{CNO}_2\text{ClCy}_2 + 4\text{AgNO}_3 + 8\text{H}_2\text{O}$ requires 34.27 p. c. silver, and 8.45 p. c. chlorine.

The compound when heated to 80° decomposes suddenly with great frothing, leaving a very bulky residuc. The water contained in it may, however, be removed by heating it under boiling water; it then fuses into dark-red drops. A quantity of cold water is then added, and the substance taken out and dried with filter-paper, and afterwards *in vacuo*.

I. .693 grm., treated with nitric acid as before, gave .259 grm. AgCl, or 9.25 p. c. chlorine.

II. Filtrate from the above, mixed with hydrochloric acid, gave .096 grm. AgCl, which, added to the former amount, is .355 grm., or 38.55 p. c. silver.

The formula $3\text{CNO}_2\text{ClCy}_2 + 4\text{AgNO}_3$ requires 38.69 p. c. silver, and 9.53 p. c. chlorine.

A compound very similar in appearance is formed with nitrite of silver. It is, however, more stable, sustaining the heat of the water-bath without decomposition.

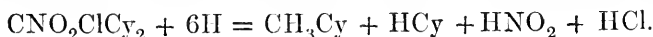
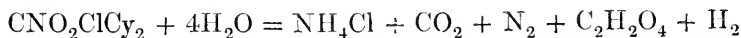
The original substance, as before mentioned, is very unstable; its watery solution slowly deposits solid products, with evolution of gas-bubbles, and on heating with acids or alkalis, the decomposition is very rapid, and appears to be mainly the same in both cases. When an alkali is used, however, the mixture becomes very dark, and large quantities of the azulmic compounds are formed. The most definite reaction is obtained by heating the

watery solution with a few drops of dilute nitric acid, when it rapidly becomes lighter in colour, and a large quantity of gas is given off with effervescence, the products of the decomposition giving additional evidence of the composition of the substance.

In the remaining solution was found a considerable quantity of oxalic acid, recognized by the usual tests, and by the analyses of a lead and a barium salt.

The gas given off consists principally of carbonic acid and nitrogen, containing also vapour of hydrocyanic acid. After treatment with potash, the remaining nitrogen was found to be slightly inflammable. On passing it over red-hot oxide of copper, water was deposited in the front of the tube, and the gas collected over mercury contained a further quantity of carbonic acid. Another portion passed through an empty tube heated to redness gave a quite appreciable quantity of hydrocyanic acid. From these indications it may be concluded that the inflammability of the gas is owing to the presence of vapour of methylic cyanide.

The following equations represent the two reactions, which appear to take place at the same time :—



In addition to these main products of the action of acids on the substance, I have, by extracting the neutralised solutions with ether, obtained small quantities of at least three solid crystalline bodies containing carbon, hydrogen, chlorine, oxygen, and high per centages of nitrogen; but I can only indicate the existence of these bodies, the separation and purification of which were found to be unusually difficult, both from the nature of the substances, and the very minute quantities formed.

In conclusion, my best thanks are due to Mr. John Williams for the preparation of the greater part of the chloropierin used in these experiments.

XXXV.—*Note on the Hydrocarbons contained in crude Benzol.*

By C. SCHORLEMMER.

By treating with concentrated sulphuric acid the light oils formed in the destructive distillation of cannel-coal at a low temperature, I obtained a series of hydrocarbons of a high boiling point, having the general formula $2(C_nH_{2n-2})$, which, as I have pointed out in a communication to the Royal Society, are formed by the condensation of hydrocarbons of the acetylene series C_nH_{2n-2} *. I have found that these hydrocarbons are also contained in the oils obtained in the manufacture of coal-gas, which consist chiefly of the members of the benzol series. A large quantity of crude benzol was obtained by fractional distillation, which boiled between 80° — 82° C. Bromine was added, as long as its colour disappeared. The bromides thus formed could not be separated completely from the benzol by distillation, as they undergo decomposition with evolution of hydrobromic acid and separation of carbonaceous matter, even below the boiling point of water. The greater portion of the benzol was therefore removed at as low a temperature as possible, and the remaining mixture heated with sodium. The mixed hydrocarbons thus obtained were again treated with bromine and then distilled. As soon as the benzol had distilled over, the temperature rose quickly up to 200° C., and between this temperature and 220° C. the remaining liquid came over. This liquid, which on analysis was found to contain 64.3 % Br., is a mixture of several bromides, the greater portion of which consists of $C_6H_{10}Br_2$ (66.1 % Br.). On adding an excess of bromine, heat is evolved, and after some time, white needle-shaped crystals separate out, the quantity of which increases for some days, until nearly the whole is converted into a solid mass. By washing with cold alcohol, in which the crystals are only sparingly soluble, the excess of bromine and the liquid bromides (bromides of hexylene and heptylene) can be removed, and on recrystallisation from boiling alcohol, perfectly white needles are obtained, sometimes several inches long, which melt at 112° C., and distil without

* Proc. Roy. Soc. xv, 132.

decomposition at 318°C . (corrected). Their composition is $\text{C}_6\text{H}_{10}\text{Br}_4$, as the following bromine determination shows:

0.1970 substance gave 0.3612 bromide of silver and 0.0043 metallic silver.

Calculated for $\text{C}_6\text{H}_{10}\text{Br}_4$.
79.60 % Br.

Found.
79.64 % Br.

From these experiments it follows, that crude benzol contains (besides members of the olefine series) the hydrocarbon C_6H_{10} , which is very likely identical with hexoylene, described by Caventon,* which boils at 80° — 85°C . These hydrocarbons, which combine directly with bromine, adhere obstinately to benzol, even when it has been purified by treatment with concentrated sulphuric acid, and by repeated freezing and pressing out the portion of the remaining liquid; they may, however, be removed by adding bromine, as long as its colour disappears, treating with caustic potash and rectifying. A perfectly pure benzol may thus be obtained, boiling constantly at 81°C ., which gives a nearly colourless nitro-benzol and dissolves in pure concentrated sulphuric acid with hardly any coloration. The oils obtained from gas-tar contain the hydrocarbons of the acetylene series in a much smaller proportion, than those formed in the distillation of cannel coal at a low temperature. I am at present engaged in experiments to isolate these hydrocarbons from Boghead naphtha.

XXXVI.—*Note on Ethyl-hexyl Ether.*

By C. SCHORLEMMER.

WHEN chloride of hexyl is heated in a sealed tube with an alcoholic solution of potash, chloride of potassium separates out; and on adding water to the liquid, a light oil is obtained, which according to Cahours and Pelouze† consists chiefly of hexylene, but also contains other substances. In the preparation of hexylene according to this method, I obtained some quantity of a liquid of a higher boiling point, which on fractional distillation over sodium (in order to remove traces of alcohol) was found to con-

* Compt. rend. lix, 449.

† Ann. Ch. Phys. (4), i, 27.

sist almost entirely of a compound boiling constantly at 131° — 133° , and which on analysis gave numbers agreeing with the formula $C_8H_{18}O$;

0.4385 substance gave 1.190 carbonic acid and 0.549 water.

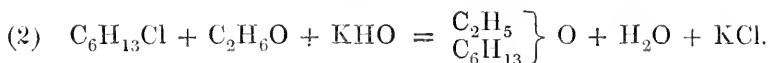
	Calculated.		Found.
C_8	96	73.85	74.0
H_{18}	18	13.85	13.9
O	16	12.30	
	<hr/>	<hr/>	<hr/>
	130	100.00	

The mode of preparation shows that this substance is ethyl-hexyl ether $\left. \begin{matrix} C_2H_5 \\ C_6H_{13} \end{matrix} \right\} O$.

Ethyl-hexyl ether is a colourless, mobile, highly refracting liquid, possessing a strong ethereal smell resembling that of ethyl-amyl ether. The specific gravity was found to be—

$$\begin{aligned} \text{At } 16^{\circ}5 \text{ C} &= 0.7752 \\ \text{,, } 30^{\circ} \text{ ,,} &= 0.7638 \\ \text{,, } 63^{\circ} \text{ ,,} &= 0.7344 \end{aligned}$$

By acting on chloride of hexyl with an alcoholic solution of potash, two reactions, therefore, take place, viz.:—



The latter reaction corresponds to Berthelot's mode of the formation of common ether by treating bromide of ethyl with an alcoholic solution of potash,* and to Balard's reaction for the production of ethyl-amyl ether by acting with the same re-agent upon iodide of amyl,† and also to Guthrie's mode of preparing ethyl-amyl ether by heating iodide of ethyl with a solution of caustic potash in amyl alcohol.‡

* Ann. Ch. Pharm. xcii, 351.

† Ann. Ch. Phys. [3], xii, 302. Balard considered this ether as amyl ether and some French chemists still adhere to this opinion (*vide* Frémy et Pelouze, *Traité de Chimie* v, 524) although Williamson pointed out its true constitution many years ago.

‡ Phil. Mag. (4) xiv, 186.

XXXVII. — *On the Reduction of the Oxides of Nitrogen by Metallic Copper in Organic Analysis.*

By W. THORP.

SOME years ago, in a paper published by Dr. Frankland ("Philosophical Transactions," vol. 147, page 63), some determinations of nitrogen in organic bodies by Dumas's method were given, in which it was found that a certain quantity of the nitrogen was evolved from the combustion-tube as nitric oxide, notwithstanding that a considerable quantity of metallic copper was placed in the anterior portion of the tube. The author states that—
 "It was found impossible to prevent the occurrence of a considerable amount of binoxide of nitrogen in the resulting gas. Even when it was made to stream over 12 inches of an intensely ignited mixture of copper turnings and copper reduced from the oxide, the resulting nitrogen still contained 10·9 per cent. of binoxide. It was, therefore, necessary to estimate the volume of the latter gas by means of solution of protosulphate of iron, and to deduct half its volume from the observed amount of the mixed gases. The presence of protoxide of nitrogen would not interfere with the accuracy of the result, as this gas is unaffected by solution of protosulphate of iron, and contains exactly its own volume of nitrogen."

These analyses having been conducted in the ordinary charcoal furnace, it appeared probable that the oxides of nitrogen might be decomposed by metallic copper under the influence of the superior temperature obtainable in Hofmann's gas combustion furnace. It was to decide this question that the following experiments were undertaken:—

Some thin bands of copper, about 3·5 mm. wide, obtained by passing stout copper-wire between rollers, were made into spirals, about 200 mm. in length, by twisting them round a glass rod. Two of these spirals, placed one within the other, were introduced into a piece of combustion-tube. Oxygen was next passed through the tube while heated to redness, in order to convert the copper superficially into oxide, which was afterwards reduced by a current of dry hydrogen. When the reduction was complete, the tube was allowed to cool, the stream of hydrogen being continued.

Before commencing each of the undermentioned experiments, the hydrogen was expelled by a stream of carbonic anhydride, and the conditions under which nitrogen determinations are usually made were, to a certain extent, obtained by mixing nitric oxide with about twice its volume of carbonic anhydride.

In experiments I and II, the copper was heated to bright redness, the mixture of nitric oxide and carbonic anhydride passed over it, and the gas issuing from the tube collected over mercury in a graduated receiver about 460 mm. in length, and about one-sixth filled with a strong solution of potassic hydrate. The flow of gas was so regulated that about two cubic centimetres were collected per minute.

After remaining for some time in contact with the alkaline solution, the volume of gas was read off, a measured quantity of oxygen added, and the mixture allowed to stand during several hours. The volume was again observed, and, no diminution having taken place, it was evident that the whole of the nitric oxide had been decomposed.

	I.			II.			
	Gas collected.	Oxygen added.	Mixture after adding oxygen.	Gas collected	Oxygen added.	Mixture after adding oxygen.	
Observed volume ..	54·6	13·75	63·2	93·1	9·11	104	cub. cent.
Temperature of gas.	16°·5	16°·5	14°·8	21°	21°	18°·4	C.
Barometer	758·25	758·25	764·15	758·5	758·5	759·7	mm.
Temperature of do. .	16°·7	16°·7	13°·6	19°·6	19°·6	16°·9	C.
Aqueous column....	78	..	77	80·8	..	12·8	mm.
Mercurial	104	79·7	60	7	48·7	38	mm.

These numbers reduced to 760 mm. B. and 0° C. give—

	I.	II.
Gas collected	42·639	82·252 c.c.
Oxygen added	11·299	7·683 „
	<hr/>	<hr/>
Vol. of mixture after adding oxygen	53·938	89·935 „
	<hr/>	<hr/>
Difference	0·205	0·088

III. Another experiment was made, in which the tube was

heated to dull but distinct redness, all other conditions being as in the previous experiments. On observing the volume after the addition of oxygen, a considerable absorption was found to have taken place. In order to ascertain the amount of oxygen absorbed, the residual portion was determined by means of pyrogallic acid.

	Gas collected.	Oxygen added.	Mixture after adding oxygen.	Residue after adding pyrogallic acid.	
Observed volume ..	72·6	31·55	87	61·6	cub. cent.
Temperature of gas .	22°·8	22°·8	23°·2	24°·4	C.
Barometer	761·4	761·4	759·9	759·25	mm.
Temperature of do..	21°·4	21°·4	22°·6	23°·3	C.
Aqueous column ...	74	..	96	130·8	mm.
Mercurial „ ...	40·2	8·8	14·8	27·9	mm.

These numbers reduced to 760 mm. B. and 0° C. give—

Gas collected	60·789	cub. cent.
Oxygen added	27·933	„
	<hr/> 88·722	„
Vol. of mixture after adding oxygen	74·945	„
	<hr/> 13·777	„
Volume absorbed	13·777	„
Residue after adding pyrogallic acid	51·597	„

By deducting this remaining nitrogen from the volume of the gas collected, we find that the latter contained 9·192 cub. cent. of nitric oxide. As this gas consists of equal volumes of nitrogen and oxygen, it follows that 51·597 of nitrogen was collected as such, and 4·596 as nitric oxide, that is, 8·179 per cent. of the nitrogen, in the gas acted upon, escaped reduction.

IV. In the next experiment, the mixture of nitric oxide and carbonic anhydride was passed so that about 4 cub. cents. were collected per minute, other conditions being the same as in experiments I and II.

	Gas collected.	Oxygen added.	Mixture after adding oxygen.	Residue after adding pyrogallie acid.	
Observed volume...	66·1	25·84	83·9	64·2	cub. cent.
Temperature of gas.	21°·6	23°·3	23°	21°·8	C.
Barometer	764·65	763·5	762·6	762·05	mm.
Temperature of do..	20°·5	22°·6	21°·7	20°·3	C.
Aqueous column....	71·3	..	70·9	132	mm.
Mereurial „	63	25·3	17·8	101·3	mm.

These numbers reduced to 760 mm. B. and 0°C. give:—

Gas collected	54·147	cub. cent.
Oxygen added	22·363	„
	76·510	„
Vol. of mixture after adding oxygen	72·611	„
Volume absorbed	3·899	„
Residue after adding pyrogallie acid	49·000	„
Nitric oxide in the gas collected ..	5·147	„

This corresponds to 4·99 per cent. of nitrogen as nitric oxide.

V. A last experiment was performed to ascertain the influence of a much larger proportion of aqueous vapour. For this purpose about 70 mm. of the posterior portion of the tube was filled with moistened asbestos; the gases were thus charged with water before coming in contact with the heated copper, the other conditions remaining as in experiments I and II.

	Gas collected.	Oxygen added.	Mixture after adding oxygen.	Residue after adding pyrogallie acid.
Observed volume...	57	24·55	74·4	54·2
Temperature of gas.	18°·2	18°·2	20°	21°·9
Barometer	752·75	752°·75	750·95	750·25
Temperature of do..	17°	17°	19°	20°·6
Aqueous column....	95·5	..	103·1	154
Mercurial „	78·3	32	8·6	30·9

These numbers reduced to 760 mm. B. and 0°C. give:—

Gas collected	45·425	cub. cent.
Oxygen added	21·286	„
	<hr/>	
	66·711	„
Mixture after adding oxygen	61·861	„
	<hr/>	
	1·850	„
Residue after adding pyrogallie acid	45·085	„
Nitric oxide in the gas collected....	0·31	„

This corresponds to 3·756 per cent. of nitrogen as nitric oxide.

This last experiment seems to show that the complete reduction of the oxide of nitrogen cannot be depended upon in an actual analysis where much aqueous vapour is usually present. But 3·756 represents the percentage of the *nitrogen* which escapes reduction, and in an actual analysis, even if the substance burnt contained 20 per cent. of nitrogen, the error would only be 0·75 per cent., which would not very materially affect the results.

The conclusion I would draw from these results is that at a moderate rate of speed, and at a high temperature, practically, the whole of the nitrogen is evolved as such in Dumas's method of determination.

These experiments were conducted in the laboratory of the Royal College of Chemistry, and under the kind superintendence of Dr. Frankland.

XXXVIII.—On Nitro-Compounds. Part II. Appendix.

By EDMUND J. MILLS, D.Sc., F.C.S.

WHILE occupied with my experiments on nitrobenzoic acid, which have already appeared in the Society's Journal,* several minor questions presented themselves, all having reference to the main object of the inquiry, and to which I was anxious to obtain a response. One of these points, indeed, appeared of particular importance. I had met with various substances presenting differences in chemical behaviour, fusion-point, solubility, and general appearance, which agreed nevertheless in having the composition assigned to hydric mononitrobenzoate. It was very desirable that

* Chem. Soc. J. [2] iii, 319. To that place I refer for many details of preparation and properties necessarily omitted here.

these differences should become the subject of a special investigation. The results obtained are recorded in the following sections:—

1. *Alpha Hydric Nitrobenzoate*.—This substance, prepared by the action of absolute hydric nitrate on hydric benzoate and subsequent washing with water, was dried in air and afterwards at 100° C.

0·3520 grm. substance, gave 0·6492 grm. carbonic dioxide and 0·0949 grm. water.

	Found.	$C_7H_5NO_4$.
Carbon	50·30	50·30
Hydrogen	2·99	2·99

The body was therefore pure. Its fusion-point* was next determined. The results were:—

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Fusion-point	129·9	139·2	136·4	135·2	133·8	133·8	136·7	133·0	125·7
Point of excessive heating	130	140	140	140	134	135	156	200	

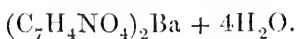
The number in the second column was obtained after a very *slow* elevation of temperature. According to another determination, in a different apparatus, the first fusion-point was 127·5.

The original body was now converted into barytic salt by boiling with water and excess of pure barytic carbonate till the liquid lost its acid reaction. The solution was filtered off and allowed to cool, when an abundant deposit of white lustrous crystals occurred. These consist of thin flattened needles, sometimes of considerable length, and united together in radiated groups,—as if the individual crystals had once been parallel, but had been caused to diverge subsequently by some powerful constriction at the centre of the bundle. After standing in contact with the supernatant liquid for twenty hours, the latter was rapidly separated by filtration; and a known volume—100 cubic centimetres—evaporated to dryness on the water-bath, and dried at 150°. At that temperature the composition of the salt is represented by the formula



while the air-dried salt (at the ordinary temperature) contains, as is well known—

* All the fusion-points mentioned in this paper were taken with the same apparatus, except in a single case which is expressly alluded to. They are also all corrected in the usual manner. Substances were dried at 100° prior to fusion.



The crystals remaining on the filter were now again dissolved in about the same volume of water as previously, cooled, allowed to stand about twenty hours, and treated as before. Five consecutive determinations were made in this way. [The columns headed "solubility" show the number of parts of water required to dissolve one part of the salt.]

Crystallisation.	Temperature.	Solubility.	
		(Anhydrous).	(Hydrous).
(1)	6·6	431·3	375·5
(2)	8·6	425·1	370·0
(3)	8·8	456·7	397·6
(4)	10·0	469·6	408·8
(5)	8·8	745·6	414·0

The barytic salt remaining after this repeated crystallisation, was converted into hydric salt by treatment with hydric sulphate, washed and dried in air. It will be again referred to in Section 5.

α -Barytic nitrobenzoate preserves its appearance almost unchanged, even after exposure to the high temperature which has rendered it anhydrous. α -Hydric nitrobenzoate melts under water on very slight heating.

2. *Beta-Hydric Nitrobenzoate*.—This is the well-known modification obtained by the action of hydric nitrate upon toluol. In my last paper, owing to an inadvertence in the mode of experimenting, the solubility of this body was much underrated. I had used the process of evaporation, supposing the substance not to be volatile with the vapour of water at 100° —an error in which Zinin appears to have shared. The following numbers have been obtained in a more satisfactory manner:—

1. A solution saturated at 16° was neutralised with calcic carbonate, the calcium precipitated from the filtrate as oxalate, and this last dried and ignited after final moistening with hydric sulphate.

200 c. c. solution gave 0·0613 grm. calcic sulphate.

2. A solution saturated at 15° , was treated with barytic hydrate in excess, then with carbonic dioxide, and filtered. The filtrate was precipitated with hydric sulphate.

372·5 c. c. solution gave 0·1957 grm. barytic sulphate.

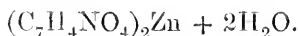
One part of this substance, accordingly, dissolves in—

I. 1327·1 parts of water at 16°.

II. 1326·5 parts of water at 15°.

Professor Abel very kindly sent me a small specimen of the hydric nitrobenzoate which he obtained* long since by the action of hydric nitrate on cumol. I purified this by boiling with chloride of lime, filtering the solution hot, and mixing the filtrate with hydric chloride. The crystals which separated on cooling were easily washed; they were then dried, ultimately at 100°, and fused. The fusion-point was 236·3. This number, owing to the mode of purifying employed, probably admits of comparison with that given for β -hydric nitrobenzoate by Willbrand and Beilstein—namely, 240°, a value which I have confirmed. The appearance of the substance is strikingly similar to that of the ordinary β variety; it also resembles the latter in the fact that it does not fuse under boiling water, and has a very slight solubility in cold water.

Zinin† and Sokoloff‡ have described a body, obtained by the action of hydric nitrate on desoxybenzoin, which they term “ β -nitrobenzoic acid,” and consider to be a new species. Zinin estimated its solubility at 1 in 1,200 parts of water at 17°, and remarks that it does not melt under boiling water. The fusion-point is not on record. Sokoloff states the solubility of his zinc salt (which crystallises in platy needles) to be 1 in 135 parts of water at the ordinary temperature, and expresses its composition by the formula



I have prepared the ordinary β -zinc salt, and find its description, so far as I can judge, to correspond with that of the body obtained by Zinin. A partial analysis and an approximate determination of its solubility are here appended.

0·4602 grm. substance, dried in the open air, gave 0·0864 grm. zinc oxide :

	Found.	$(\text{C}_7\text{H}_4\text{NO}_4)_2\text{Zn} + 2\text{H}_2\text{O}.$
Zinc	15·07	15·01

15 c. c. of a solution saturated at 17°, left 0·0943 grm. residue at 100°. [At this temperature the salt is probably anhydrous;

* Ann. Ch. Pharm. lxiii, 313.

† Ann. Ch. Pharm. cxxvi, 223.

‡ Bull. Imp. Acad. St. Pet., vii, 476.

heated further, it begins to decompose.] One part of this substance, therefore, calculated as hydrous salt, dissolves in

152·7 parts of water at 17°.

Sokoloff, who did not heat the residue, has probably given too low a result.

The potassic (β) nitrobenzoate, also, which I have prepared, resembles naphthalene.

3. Gamma Hydric Nitrobenzoate.—When hydric benzoate is digested for a short time at about 100° with the ordinary nitro-sulphuric mixture, there is produced, on adding water, a white precipitate differing from the two preceding bodies in certain particulars, but agreeing with them in composition. I distinguish it, provisionally, by the name which precedes this section.

The barytic salt was prepared in the manner already described, and the barium determined in a specimen dried in the open air.

0·5290 grm. gave, on evaporation with hydric sulphate and ignition, 0·2283 grm. barytic sulphate.

	Found.	$(C_7H_4NO_3)_2Ba + 4H_2O$.
Barium	25·37	25·32

Successive crystallisations and determinations of solubility were then resorted to, the latter being made on volumes varying from 30 to 150 c. c., and the residue dried at 150°.

Crystallisation.	Temperature.	Solubility.	
		(Anhydrous).	(Hydrous).
(3)	15·0	437·1	380·5
(4)	14·5	442·1	384·8
(5)	21·0	414·7	361·0
(6)	17·0	421·6	367·0

This salt can scarcely be said to be distinguishable in appearance from the α -nitrobenzoate. The mother-liquid of the second crystallisation was made to yield hydric salt as before, and this was submitted to fusion.

	(1)	(2)	(3)	(4)	(5)
Fusion-point	135·9	140·5	142·6	142·9	134·7
Point of excessive heating	136	141	153	153	—

The fusion-point of another preparation was 135·7. A specimen made from the sixth crystallisation of the barytic salt gave the consecutive numbers 132·5, 141·3. If the action of the nitro-

sulphuric mixture be continued for four hours the fusion-point of the nitrobenzoate so produced may be 141° .

The hydric salt melts easily under hot water.

Note.—The presence of a small quantity of hydric benzoate is well known to lower the fusion-point of hydric nitrobenzoate. Although I was satisfied by analysis that barytic benzoate was absent from the barytic salts I had prepared, or, at any rate, that its amount was perfectly inappreciable, it seemed that an estimation of the solubility of barytic benzoate might *possibly* not be without importance. The substance was prepared from sublimed hydric benzoate and pure barytic carbonate, and twice crystallised; the solution was neutral and saturated.

30 c. c. at $8^{\circ}3$ gave 0.8853 grm. barytic sulphate.

15 c. c. at $9^{\circ}1$ left 0.7225 grm. benzoate at 110° C.

1 part of the anhydrous salt, therefore, dissolves in—

20.83 parts of water at $8^{\circ}3$ C.

20.76 „ „ $9^{\circ}1$ C.

4. *Delta Hydric Nitrobenzoate.*—After the separation of the preceding hydric salt by means of water, the mother-liquid is allowed to repose for some time, filtered if necessary, and exactly precipitated by means of barytic carbonate, nitrate, or hydrate. On again filtering and evaporating to dryness, a residue is obtained, the amount of which is proportional to the length of the original digestion. It has the composition of hydric nitrobenzoate. It is best purified, first by pressure, then by conversion into barytic salt, which is washed with successive *small* quantities of cold water and crystallised. In this way a yellow colouring matter and some adhering hydric nitrate are removed. The hydric salt can be prepared in the usual way. It melts readily under hot water.

The barytic salt, made from hydric salt at the third crystallisation, was submitted to a partial analysis, after drying in the open air.

0.1718 grm., evaporated with hydric sulphate and ignited, gave 0.0747 grm. barytic sulphate.

	Found.	$(C_7H_4NO_4)_2Ba + 4H_2O$.
Barium	25.57	25.32

The solubility of this salt was as follows:—

45 c. c. of a solution saturated at $9^{\circ}7$ left 0.1266 grm. residue at 150° .

Accordingly, 1 part of the anhydrous salt dissolves
 in 359.3 parts of water } at $9^{\circ}7$.
 1 part of the hydrous salt dissolves in
 309.3 parts of water }

Another preparation* of the barytic salt, after three crystallisations, was treated in the same manner.

0.3398 grms. gave 0.1456 grm. barytic sulphate.

	Found.	$(C_7H_4NO_4)_2Ba + 4H_2O$.
Barium	25.19	25.32

The determinations of solubility were made on 15—30 c. c. of solution.

Crystallisation.	Temperature.	Solubility.	
		(Anhydrous).	(Hydrous).
(5)	16	303.9	264.5
(6)	16	351.7	305.2
(7)	13	394.5	343.4

The above salt crystallises in forms much resembling those assumed by α and γ nitrobenzoate. The component crystals, however, of each group are much thicker and are terminated by less acute angles than in the other two cases; the groups themselves, also, are of relatively much smaller size.

The fusion-point of the hydric salt was determined on a specimen which had been thrice crystallised and was quite white.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Fusion-point	140.8	140.1	140.3	140.7	140.9	141.5	140.9	140.9	140.4	141.3
Point of excessive heating }	—	142	141	141	150	160	160	170	170	—

The first fusion-point has been confirmed by other determinations. The amount of crude substance originally obtained precludes the serious influence of any traces of the γ modification which might be supposed present.

(5). *Action of heat on α Hydric Nitrobenzoate and on Barytic Nitrobenzoates.*— α hydric nitrobenzoate, prepared from the barytic salt at the fifth crystallisation, was heated to 137° , and maintained at that temperature for a few minutes; it had fused

* For this specimen I am indebted to my friend Mr. John Ferguson.

long previously. After rapid cooling it was converted into barytic salt, and the solubility of this was determined.

30 c. c. of a solution saturated at $14^{\circ}5$ left 0.0913 gm. residue at 150° .

Accordingly, 1 part of the anhydrous salt dissolves	} at $14^{\circ}5$.
in 328.5 parts of water	
1 part of the hydrous salt dissolves in	
286.9 parts of water	

γ and δ barytic nitrobenzoates change somewhat on heating to 150° . Residues from various determinations of the solubility of these salts were dissolved in water and crystallised; the mother-liquids contained bodies of greater solubility than the original nitrobenzoates, especially in the latter case.

(γ) 50 c. c. of a solution saturated at $19^{\circ}7$ left 0.1296 gm. residue at 150° . Solubility (of supposed anhydrous salt) 1 in 385.1 parts of water.

(δ) 15 c. c. of a solution saturated at 15° left 0.0784 gm. residue at 150° . Solubility (of anhydrous salt) 1 in 191.3 parts.

A yellow coloration accompanies this change. On the other hand, α barytic nitrobenzoate shows scarcely a sign of alteration under these circumstances.

Observations.

The experiments recorded in (1), (3), and (4), taken in connection with those described in my previous paper, show that there are bodies having the composition of hydric nitrobenzoate which melt at temperatures ranging from 128° to 141° . The disputed number (127°) given by Mulder is therefore confirmed, *although* the substance with which he worked was not free from hydric benzoate.

The fusion-point of these bodies evidently rises with the amount of force expended in their preparation; and their barytic derivatives decompose more easily the more preliminary work has been done upon them. When hydric nitrate is made to act upon hydric benzoate, the first nitrobenzoate obtained melts at about 128° . But, even here, if the action be considerably prolonged, the fusion-point may rise (as I had already shown) to 137.5° . Hydric benzoate (or the nitro-benzoate obtained by the first process) when treated with the ordinary nitro-sulphuric mixture for a short time, is transformed into a hydric nitro-benzoate fusing at

136°. Lastly, if this reaction be prolonged in its turn, a third nitrobenzoate is produced, melting at 141°.—Heat alone acts in a similar manner. It is shown in (1) that the fusion-point of the α -modification is much higher after the substance has been heated, and decidedly approximates towards that of the δ -modification. The same is true of the γ variety (3). Moreover the α nitrobenzoate, after a short and gentle fusion, yields a barytic salt which, in its solubility, strikingly accords with the δ -salt.

Naumann* has made some careful experiments on the fusion-point of hydric nitro-benzoate, which have led him to doubt Mulder's result. The bodies which yielded the number he mentions (141°) had, however, been submitted to repeated heating and a train of processes. A high fusion-point is precisely what might have been expected.

It will be noticed that the pure barytic salts (α and δ) are even unable to retain a constant solubility on repeated crystallisation; the γ -salt, on the other hand, exhibits a surprisingly perfect stability under the circumstances.

Such transformations under the influence of heat are already numerous and familiar. Those which are now recorded appear to resemble most closely, in the suddenness and minuteness of the effect, the corresponding changes observed by Duffy† in certain fats.

I will now compare the nitrobenzoates I have discussed.

α . The hydric salt melts first at about 128°. It yields a barytic derivative, which is but imperfectly stable on repeated crystallisation, less liable to decompose on heating than the α and γ barytic salts, more soluble than the γ salt, less soluble than the δ salt.

γ . The hydric salt melts first at about 136°. It yields a barytic derivative which is perfectly stable on repeated crystallisation, more liable to decompose on heating than the α -, but less so than the δ -salt; and less soluble than the α - or δ -salt.

δ . The hydric salt melts first at 141°. It yields a barytic derivative which is imperfectly stable on repeated crystallisation; more liable to decompose on heating than the α - or γ -salt; more soluble than those two bodies; and also different from them in that its crystalline groups are of smaller absolute size, and the individual crystals have less acute angles.

* Ann. Ch. Pharm. cxxxiii, 206.

† Chem. Soc. Qu. J. v. 179.

These differences find a parallel in the case of α - and β -lutidine described by Mr. Greville Williams*; and those bases also exhibit the striking resemblances which obtain among the above hydric nitrobenzoates.— β hydric nitrobenzoate is already well known as a definite species; it differs by the broadest characters from those which precede. I will only remark that it appears likely from (2) that the substance obtained by Abel, and that described by Zinin and Sokoloff are identical with what I had examined under the name " β -nitrobenzoic acid," and which had been termed "nitrodiacylic acid" by other authors.

Finally, it will appear that the hydrogen in hydric benzoate is in such a condition that it is most minutely susceptible to the action of reagents. Three hydric chlorobenzoates are known,† in addition to the derivatives to which I have paid attention. We may legitimately suppose the most mobile of elements in the free state to preserve its character, to a certain extent, when combined; and in this respect, hydric benzoate only repeats on a more extensive scale what I have shown to be true for marsh-gas.‡

My best thanks are due to Professor Williamson for the use of his laboratory.

XXXIX.—*Contributions to the Notation of Organic and Inorganic Compounds.*

By E. FRANKLAND, F.R.S.

THE typical formulæ generally used to represent the different great families of organic compounds are far from fulfilling their functions in an equally perfect manner. Of the types in general use, those employed in the formulation of the artificial organic bases and the organo-metallic bodies are alone satisfactory; on the other hand, the water, hydrochloric acid, and hydrogen types fail more or less completely to give an intelligent representation of the atomic arrangement of the bodies which are formulated upon them.

The cause of this comparative success in the one case and failure

* Proc. Roy. Soc. 1864, 303.

† Ann. Ch. Pharm. cxxxiii, 241.

‡ Chem. Soc. J. [2] ii, 163.

in the other is doubtless to be found in the almost exclusively synthetical origin of the alkaloidal and organo-metallic compounds. The number and nature of the constituent radicals of these bodies became thus invested with a degree of certainty which, until recently, was almost entirely wanting in other families of organic compounds.

The rapid progress that has of late been made in the application of synthetical methods to the production of most of the other great organic families, has rendered it possible to apply, with some prospect of success, a mode of notation, the principles of which were suggested in a lecture which I delivered at the Royal Institution in the year 1858.* This method was founded upon the carbonic acid, or, as it is now sometimes called, the marsh-gas type. The adoption of this type was, however, nothing more than the application to the compounds of the tetrad carbon atom, of the principles which I had previously employed in the notation of organo-metallic bodies containing metals of various degrees of atomicity.† As examples of the application of this mode of notation to some of the chief organic families, the following may be adduced:—

Alcohols.	Ethers.	Fatty acids.	Aldehydes.	Ketones.
$\text{C}^{\text{iv}} \begin{Bmatrix} \text{CH}_3 \\ \text{H} \\ \text{H} \\ \text{OH} \end{Bmatrix}$	$\text{C}^{\text{iv}} \begin{Bmatrix} \text{CH}_3 \\ \text{H} \\ \text{H} \\ \text{OC}_2\text{H}_5 \end{Bmatrix}$	$\text{C}^{\text{iv}} \begin{Bmatrix} \text{CH}_3 \\ \text{O} \\ \text{OH} \end{Bmatrix}$	$\text{C}^{\text{iv}} \begin{Bmatrix} \text{CH}_3 \\ \text{O} \\ \text{H} \end{Bmatrix}$	$\text{C}^{\text{iv}} \begin{Bmatrix} \text{CH}_3 \\ \text{O} \\ \text{CH}_3 \end{Bmatrix}$
Ethylie alcohol.	Ethylie ether.	Acetic acid.	Acetic aldehyde.	Acetone.

The meaning of these formulæ is so obvious as scarcely to require description; that of ethylie alcohol, for instance, represents an atom of tetrad carbon united first to the carbon of methyl, secondly to each of two atoms of hydrogen; and lastly, to oxygen, the latter dyad element being likewise united to an atom of hydrogen, which is thus linked, as it were, to the first carbon atom without being actually united with it. This is a true representation of the internal arrangement of the atoms composing alcohol, not, indeed, of their relative positions with regard to each other in space, but of the mode in which they are held together. Thus of the six atoms of hydrogen in alcohol, two only are united with the atom of carbon which, in the formula, is placed to the left of

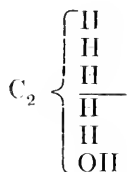
* Proceedings of the Royal Institution, vol. ii, page 540.

† Phil. Trans. for 1852, page 441.

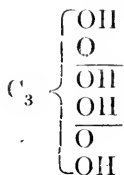
the bracket. Of the remaining atoms of hydrogen, three are united with the second atom of carbon forming methyl, whilst the sixth is combined with oxygen. Each of these atoms has, without doubt, its own proper motion—vibratory or otherwise,—besides another motion common to the whole molecule; but the formula indicates certain chemical bounds, beyond which no atom can pass without causing decomposition of the compound. Thus, confining our attention to the hydrogen, the two atoms of this element in combination with the carbon to the left of the bracket are free to move about or in the neighbourhood of that carbon-atom. In like manner the three atoms of hydrogen in the methyl are free to move around or about the methylic carbon, so long as they do not escape from the dominion of their own peculiar atom of carbon. Of precisely the same nature is the bond between the remaining atom of hydrogen and the oxygen with which it is combined. The formula proclaims, however, that all these atoms of hydrogen must remain exclusively under the domination of their respective carbon and oxygen atoms so long as the compound continues to exist. Such a formula does not deny the exercise of a certain influence by each individual atom over every other atom in the compound, but it does not allow the conception of an exchange of the atom of hydrogen, for instance, in union with oxygen, for one of the atoms of hydrogen in union with carbon, without the application of an external force and the disruption of the compound. The formula asserts such an exchange to be just as impossible as the wandering of a satellite from planet to planet in our own solar system. On no other hypothesis than this of limited mobility can the facts of isomerism receive an intelligent explanation. Dibromosuccinic acid and iso-dibromosuccinic acid could not otherwise exist separate from each other, because the one would be every moment changing into the other, and consequently both fumaric and maleic acids ought to yield, when treated with bromine, the same product, viz. : a mixture of dibromosuccinic and iso-dibromosuccinic acids. Experiment proves however that fumaric acid gives dibromosuccinic acid alone, whilst maleic acid always gives iso-dibromosuccinic acid. It would be equally impossible for lactic and paralactic acids, and for itaconic, citraconic, and mesaconic acids to exist alone; in fact the conception of isomerism in vast numbers of cases becomes impossible, except on the assumption of limited mobility of the atoms of a chemical compound. This idea of limited atomic mobility, which is one of the fundamental bases of

constitutional formulæ, forms the essential difference between constitutional and merely typical formulæ.

The constitutional formulæ above given as examples may, of course, be written in several other ways, with the retention of the same fundamental ideas of internal arrangement. Thus ethylic alcohol may be written—



In this formula the two atoms of tetrad carbon united to each other, as expressed also in the previous formula, by one bond or equivalence of each, become hexadic with regard to the remaining elements of the compound, which are placed on the right of the bracket. The way in which these elements are distributed to each of the two atoms of carbon is shown by the horizontal line. Upon the same plan the formula of mesoxalic acid is thus written—



In this compound the three atoms of carbon by union with each other thus, C—C—C, form, taken together, an octadic group, the first and third atoms being each united with oxygen and hydroxyl, forming two atoms of oxatyl; whilst the second atom, which has obviously only two bonds free for union with other elements, is saturated by two atoms of hydroxyl. Such formulæ have been used by Mr. Duppa and myself in expressing the constitution of bodies belonging to the acetic, lactic, and acrylic series of acids.* Their simplicity, as symbolic expressions of ideas regarding the constitution of organic bodies, leaves little to be desired; but, although perhaps less unwieldy than some formulæ which have been written upon the so-called mixed types, they are sufficiently so to be open to serious objection. To obviate this defect I have

* Proceedings of the Roy. Soc. p. xiii, 140; xiv, 17, 79, 83, 191, 197; xv, 25. Chem. Soc. J. [2], iii, 133, and Phil. Trans. vol. clvi., p. 37.

devised a modified notation, by which the same structural ideas can be expressed in a more condensed form, without impairing either the simplicity or the structural character of the formulæ. I have also proved its practicability by using it, both for organic and inorganic compounds, throughout my course of lectures at the Royal College of Chemistry last autumn.

In this system of notation special symbols are employed for most compound radicals, so as to render the formulæ more compact, and to avoid the too frequent use of parentheses, which always give a confused appearance to a formula. Thus ethyl is expressed by Et instead of (C_2H_5) . Many of the symbols necessary for this purpose are already in common use, such as

Me = Methyl	Pr = Propyl
Et = Ethyl	Bu = Butyl
All = Allyl	Ay = Amyl.

These symbols of the monad alcohol-radicals, with the marks of atomicity proposed by Odling, are further employed to designate the derived dyad, triad, &c., radicals, thus:—

Me'' = CH_2	or Methylene
Me''' = CH	or Formyl
Et'' = C_2H_4	or Ethylene.
&c.	&c. &c.

These compound radicals, especially the monads, are frequently linked to other elements by oxygen; thus in acetic

ether $C \begin{cases} \text{Me} \\ \text{O} \\ \text{OEt} \end{cases}$ ethyl is linked to carbon by oxygen. In all such

cases I propose to consider the radical and linking oxygen as a new compound radical. These radicals may be named *hydroxyl*, *methoxyl*, *ethoxyl*, &c., and they are symbolically represented by attaching the small letter o to the symbol of the constituent basylous radical, thus—

Ho = HO	= Hydroxyl	Meo'' = CH_2O_2	= Methyleneoxyl
Meo = CH_3O	= Methoxyl	Meo''' = CHO_3	= Formoxyl
Eto = C_2H_5O	= Ethoxyl	Eto'' = $C_2H_4O_2$	= Ethyleneoxyl
&c.	&c.	&c.	&c. &c.

The use of any but the monad organic oxy-radicals is extremely rare.

The following are the names and formulæ of the inorganic radicals employed :—

	Atomic formulæ.	Symbols.
Hydrosulphyl	HS	HS
Ammonium	NH ₄	Am
Ammonoxyl	NH ₄ O	Amo
Amidogen	NH ₂	Ad

In addition to these, the compounds of metals with the oxygen by which they are linked to other elements, compounds analogous to methoxyl, ethylenoxyl, &c., are also symbolized as radicals by the addition of the small letter o to the symbol of the metal, thus—

	Atomic formulæ.	Symbols.
Potassoxyl	KO	Ko
Zincoxyl	Zn''O ₂	Zno''
&c.	&c.	&c.

It is not necessary to dignify all these metallic compound radicals with names; but it must be borne in mind that the number of atoms of oxygen in any radical of this class depends upon its atomicity; thus a monad contains only one atom of oxygen, a dyad two, and a triad three atoms of oxygen. The use of any but monad and dyad metallic compound radicals is very rare.

In writing the formula of any compound upon this system, the symbol of the element possessing the highest atomicity is, as a rule, placed first, that is to the left, and the element so represented is always considered to be directly united with all the *active bonds* of the other elements, or compound radicals, following upon the same line; thus the formula of sulphuric acid (**S**O₂HO₂) signifies that the hexad atom of sulphur is combined with the four bonds of the two atoms of oxygen, and also with the two bonds of the two atoms of hydroxyl; but in order to distinguish such a rational formula from a more or less empirical one, the first symbol, that is the symbol of what may be termed *the grouping element*, is printed in thick type.*

By the term *bond*, I intend merely to give a more concrete expression to what has received various names from different chemists, such as an atomicity, an atomic power, and an equivalence. A monad is represented as an element having one bond, a dyad as an

* In writing these formulæ, upon a black board for instance, this distinction is not usually necessary, because the writer, being present, can explain whether his formulæ are constitutional or not.

element possessing two bonds, &c. It is scarcely necessary to remark that by this term I do not intend to convey the idea of any *material* connection between the elements of a compound, the bonds actually holding together the atoms of a chemical compound being, in all probability, as regards their nature, much more like those which connect the members of our solar system.

The number of bonds possessed by an element, or its atomicity, is, apparently at least, not a fixed and invariable quantity; thus nitrogen is sometimes equivalent to five atoms of hydrogen, as in ammoniac chloride ($\text{N}^{\text{v}}\text{H}_4\text{Cl}$), sometimes to three atoms, as in ammonia ($\text{N}^{\text{iii}}\text{H}_3$), and sometimes to only one atom, as in nitrous oxide (ON_2). But it is found that this variation in atomicity always takes place by the disappearance or development of an even number of bonds; thus nitrogen is either a pentad, a triad, or a monad; phosphorus and arsenic, either pentads or triads; carbon and tin, either tetrads or dyads; and sulphur, selenium, and tellurium, either hexads, tetrads, or dyads.

These remarkable facts can be explained by a very simple and obvious assumption, viz., that *one or more pairs of bonds belonging to an atom of the same element can unite, and, having saturated each other, become, as it were, latent*. Thus the pentad nitrogen becomes a triad when one pair of its bonds becomes latent, and a monad when two pairs, by combination with each other, are, in like manner, rendered latent; and the hexad sulphur becomes, by a similar process successively a tetrad in triethylsulphine-iodide, and a dyad in sulphuretted hydrogen.

Adopting this hypothesis, it will be convenient to distinguish the maximum number of bonds of an element as its *absolute atomicity*, the number of bonds united together as its *latent atomicity*, and the number of bonds actually engaged in linking it with the other elements of a compound as its *active atomicity*. The sum of the active and latent atomicity of any element must evidently always be equal to the absolute atomicity. Thus in sulphuric acid ($\text{S}^{\text{vi}}\text{O}_2\text{H}_2$) the absolute and active atomicities are both = vi, therefore the latent atomicity = 0. In sulphurous acid ($\text{S}^{\text{iv}}\text{OH}_2$) the active atomicity = iv, and consequently the latent = vi - iv = ii; whilst in sulphuretted hydrogen ($\text{S}^{\text{ii}}\text{H}_2$) the active and latent atomicities are respectively ii and iv.

The apparent exceptions to this hypothesis disappear on investigation: thus iron, which is a dyad in ferrous compounds (as FeCl_2), a tetrad in cubical pyrites (FeS_2), and a hexad in ferric acid

(FeO_2H_2), is apparently a triad in ferric chloride (FeCl_3); but the vapour-density of ferric chloride shows that its formula must be doubled—that, in fact, the two atoms of the hypothetical molecule of iron (Fe_2) have not been completely separated. The formulæ of the ferrous and ferric chlorides and of ferric acid then become :

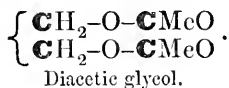
Ferrous chloride	$\text{ivFe}''\text{Cl}_2$
Ferric chloride	$''' \text{Fe}'''_2\text{Cl}_6$
Ferric acid	$\text{Fe}^{\text{vi}}\text{O}_2\text{H}_2$

Again, mercury is apparently a monad in mercurous chloride (HgCl), and a dyad in mercuric chloride ($\text{Hg}''\text{Cl}_2$); but there are strong reasons for believing that the formula of calomel ought to be doubled, in which case mercury would assume the dyad form in both compounds :

Mercurous chloride	$'\text{Hg}'_2\text{Cl}_2$
Mercuric chloride	$\text{Hg}''\text{Cl}_2$

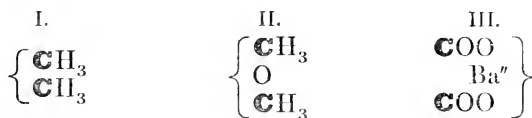
It will be remarked that the number of bonds, supposed to be combined with each other in the atom of iron in ferrous chloride, is expressed in the above symbol by the atomicity-numeral iv placed to the left of the symbol, whilst the analogous union of three bonds of each atom of iron in ferric chloride is expressed by the three dashes''' to the left of the symbol Fe_2 . I do not, however, use these co-efficients of latent atomicity, unless two or more atoms of the same element are joined together under such circumstances, that the number of bonds uniting them cannot be found by subtracting the co-efficient of active atomicity from the absolute atomicity of the element; as in hydric persulphide, hydro-sulphyl ($'\text{S}'_2\text{H}_2$), for instance, which might otherwise be viewed as $''' \text{S}'_2\text{H}_2$, or $^{\text{vi}} \text{S}'_2\text{H}_2$.

In rare cases, where oxygen links together two elements or radicals in the same line, a hyphen is placed before and after the symbol O, thus :—



The bracket has been employed in various senses in chemical formulæ, but I now propose to restrict its use to one purpose only, viz., for expressing chemical combination between two or more elements which are placed perpendicularly with regard to each

other and next to the bracket in a formula. Thus in the following cases—

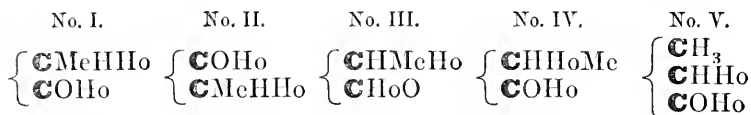


the formula No. I signifies that two atoms of carbon are directly united with each other, No. II that two atoms of carbon are linked, as it were, together by an atom of oxygen, the latter being united to both carbon-atoms, whilst in like manner No. III expresses the fact that one atom of oxygen in the formula of the upper line is linked to another atom of oxygen in the formula of the lower line, by an atom of barium.

When the elements so connected together by a bracket, are united by more than one bond, this circumstance is indicated by atomicity-marks placed to the left of the bracket, thus:

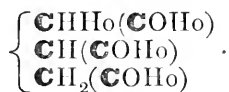


Inasmuch as no difference is at present recognised in the value of the bonds of polyad elements, the order of precedence given to the elements or radicals placed to the right of the first or grouping element of a formula is a matter of perfect indifference; and, in like manner, where the formula is written in two lines, the transposition of these lines does not affect its value. Thus all the following formulæ for lactic acid have exactly the same meaning and convey precisely the same ideas regarding the constitution of this acid:



It is nevertheless desirable to maintain as much uniformity as possible in constitutional formulæ, and I therefore propose to place oxygen-atoms next to the grouping element, to give the next precedence to alcohol-radicals in the order of their atomic weights, then to hydrogen and the metals, and lastly to place hydroxyl and analogous compound radicals, such as sodoxyl (Na_o), &c., to the extreme right, unless oxatyl comes upon the same line, in which case it is placed after hydroxyl. Thus I

always write the formula of lactic acid as in No. I, and that of citric acid as follows :—



It will be readily understood that, should it become necessary (which is far from improbable) to distinguish between the values of the different bonds of an element—of carbon, for instance—nothing would be easier than to assign such different values to the first, second, and third places after the symbol **C**.

The atomicity of an element is indicated, where necessary, according to Odling's plan; but in order to avoid the unnecessary use of atomicity-marks, I never attach them to a monad, nor to oxygen which is always a dyad. Neither need the atomicity-coefficient be attached to the tetrad element carbon, in the formulæ of organic bodies, unless this element plays the part of a dyad—an occurrence of extreme rarity. When not otherwise marked, therefore, carbon is always understood to be a tetrad.

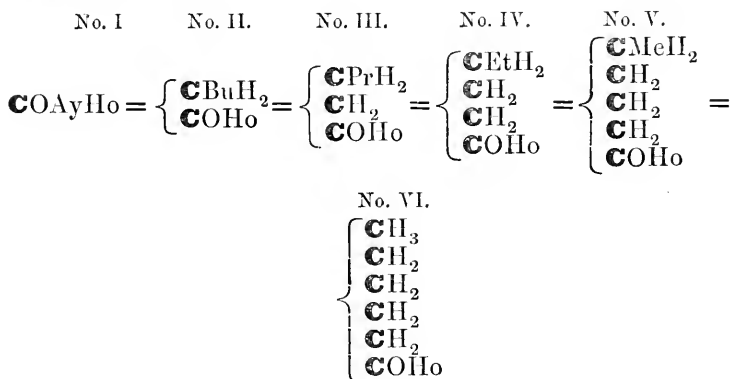
It will also, as a rule, be unnecessary to mark the atomicity of the elements which are expressed by symbols in thick type, because their atomicity is clearly indicated by the sum of the atomicities of the elements or compound radicals placed to their right, or connected with them perpendicularly by a bracket. Thus in the formula



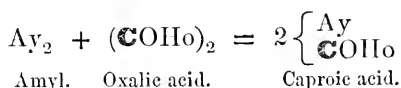
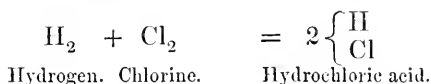
each atom of carbon is united with three atoms of the monad chlorine, whilst the bracket indicates that the two atoms of carbon are also united by one bond of each, thus stamping **C** as a tetrad element.

Whilst it is desirable for all ordinary purposes to use formulæ as compact as possible, it is not unfrequently necessary to develop them, so as to show more minute details. The system I am now describing affords peculiar facilities for such developments, since even the most compact and condensed formula contains within itself the complete history of the constitution of the compound, which can at pleasure be more minutely revealed. This quality of the new formulæ will be best rendered evident by studying an example. For this purpose we may examine the formula of caproic

acid, which may be written according to this system in any of the following ways:—



Now all these formulæ represent exactly one and the same constitutional idea. No. 1 affirms that caproic acid is composed of an atom each of amyl (Ay) and oxatyl (COHo)—a fact which may be considered as completely proved, firstly, by the synthesis of caproic acid from oxalic acid (the molecule of oxatyl $\left\{ \begin{array}{l} \text{COHo} \\ \text{COHo} \end{array} \right\}$) and amyl*; secondly, by the formation of caproic acid from amylic cyanide†; and thirdly, by the production of amyl in the electrolysis of caproic acid‡. In fact, applying Crum Brown's remark respecting the constitution of acetic acid to caproic acid, it may be as correctly said of the latter that it is a compound of amyl and oxalic acid, as that hydrochloric acid is a compound of hydrogen and chlorine, for



Reverting to the above alternative formulæ, No. 2 expresses exactly the same thing as No. 1; but in addition it partially unfolds the constitution of amyl and asserts the latter to be butylated methyl (CBuH₂)—an assertion the truth of which is proved by the

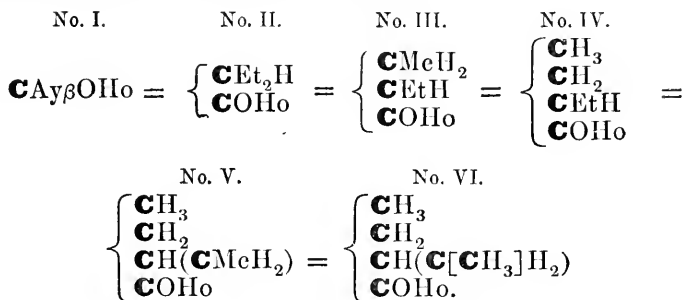
* Phil. Trans. vol. clvi, p. 341.

† Ann. Ch. Pharm. lxx, 288.

‡ Chem. Soc. Qu. J. iii, 210.

production of valerianic acid from amylic alcohol, and by the elimination of butyl in the electrolysis of valerianic acid. In like manner the remaining formulæ gradually complete the development of amyl; No. 3 affirms butyl to be propylated methyl; No. 4 represents the propyl contained in the latter as ethylated methyl; whilst No. 5 resolves ethyl into methylated methyl; and No. 6 shows the formula of caproic acid fully developed.

Of course by a process the reverse of that just described, No. 6 can, with the greatest facility, be reduced to No. 1. I find this vertical development and subsequent contraction of formulæ of considerable service in enabling students readily to comprehend the structure of very complex organic compounds, whilst it effectually guards them from the evils inseparable from the use of fixed and immutable typical formulæ. Such developments are also of value in showing the difference between normal and secondary or tertiary radicals, for compounds containing the two latter descriptions of radical cannot be fully developed vertically; thus diethacetic acid, which is isomeric with caproic acid, gives the following results on development, the isomeric amyl contained in this acid being conveniently designated by the symbol $\text{Ay}\beta$:—



A glance at these formulæ shows that at stage No. 4, diethacetic acid has reached its extreme vertical development, Nos. 5 and 6 exhibiting the complete unfolding of the atom of ethyl still remaining in No. 4, which can, however, only take place horizontally. The cause of this anomalous behaviour of bodies containing secondary and tertiary radicals is also clearly seen from No. 5, which shows that diethacetic acid contains an atom of carbon—the second from the bottom of the vertical line—which is united with *three* other atoms of carbon—a form of combination that only occurs in secondary compounds, which are thus almost infallibly detected.

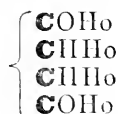
Formulae written in one line and under one dominant atom, I term *monadelphic formulae* as No. I in the above series. Those written in two lines under two dominant atoms like No. II. *diadelphic formulae*, &c. For most purposes the diadelphic form is the most useful for organic, and the monadelphic for inorganic compounds, and it is rarely necessary to employ any other, except for triacid, tetraacid, &c. alcohols and their derivatives; which, as a rule, require for their satisfactory formulation the number of lines indicated by the acidity of the alcohols. Thus glycerin and tartronic acid each require three, and tartaric acid four lines.



Glycerin.



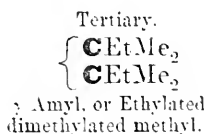
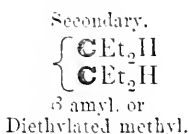
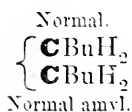
Tartronic acid.



Tartaric acid.

The following examples of the application of this mode of notation to the chief families of organic compounds will serve, better than any description, to illustrate its capabilities:

Monad Basylous Radicals.



Chlorous Monad Radicals.



Cyanogen.

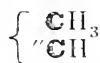


Oxatyl.

Dyad Basylous Radicals.



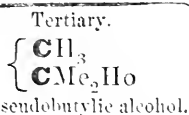
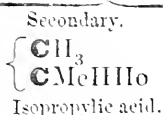
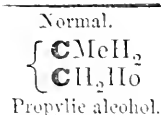
Ethylene.



Ethylidene*.

Mon-acid Alcohols.

$\text{C}_n\text{H}_{2n+1}\text{Ho}$ Series.



* For a description of the difference between these two isomers, see Phil. Trans. vol. clvi, p. 351.

$\mathbf{C}_n\mathbf{H}_{2n-1}\mathbf{H}\mathbf{o}$ Series.

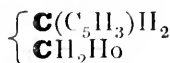
Normal.



Allylic alcohol.

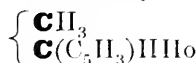
 $\mathbf{C}_n\mathbf{H}_{2n-7}\mathbf{H}\mathbf{o}$ Series.

Normal.



Benzylic alcohol.

Secondary.



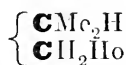
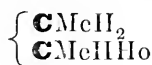
Cresylic alcohol.

The monacid alcohols of the $\mathbf{C}_n\mathbf{H}_{2n+1}\mathbf{H}\mathbf{o}$ series have been divided by Kolbe into three classes, viz.: normal (or primary), secondary, and tertiary, and doubtless both the $\mathbf{C}_n\mathbf{H}_{2n-1}\mathbf{H}\mathbf{o}$ series and the $\mathbf{C}_n\mathbf{H}_{2n-7}\mathbf{H}\mathbf{o}$ series will, when explored, be found to include corresponding divisions. A normal monacid alcohol is one which, on oxidation, exchanges two atoms of hydrogen for one of oxygen, yielding an acid containing the same number of atoms of carbon as the alcohol from which it was derived—a reaction which proves that the two atoms of hydrogen so exchanged must be in combination with the particular atom of carbon which is united with hydroxyl. This atom of carbon and its three dependents occupy the lower line of the above diadelphic formula of propylic alcohol. The transformation of a normal alcohol into the corresponding acid consequently always takes place by the conversion of the group $\mathbf{CH_2Ho}$ into oxatyl (\mathbf{COHo}), whilst the other portion of the alcohol remains entirely unaffected by the change.

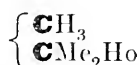
It is obvious, from an inspection of the above formula for normal propylic alcohol, that a normal alcohol may contain a secondary or even a tertiary radical. Thus if dimethacetic acid ($\begin{cases} \mathbf{CMe_2H} \\ \mathbf{COHo} \end{cases}$) were reduced to an alcohol, it would undoubtedly yield a normal alcohol, isomeric both with ordinary butylic alcohol and with Butlerow's pseudo-butylic alcohol. In like manner the action of nascent hydrogen upon methylated acetone ($\begin{cases} \mathbf{CMeH_2} \\ \mathbf{COMe} \end{cases}$) would doubtless yield isobutylic alcohol, the true homologue of isopropylic alcohol. The exact constitution of these alcohols is expressed in the following formulæ:



Normal butylic alcohol.

Normal β butylic alcohol from dimethacetic acid.

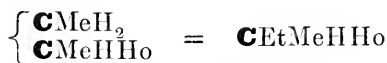
Secondary or isobutylic alcohol from methylated acetone.



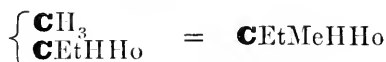
Tertiary or pseudo-butylic alcohol.

It might be asked if a body of the formula $\begin{cases} \mathbf{CH_3} \\ \mathbf{CEtHHo} \end{cases}$ would not

represent a fifth butylic alcohol. In answering such a question, the system of notation I am now describing is of especial service in preventing the possibility of an erroneous reply; it pronounces decisively that the above formula is only *apparently* different from that of isobutylic alcohol. In this and other similar cases it is only necessary to reduce both formulæ to the monadelphic type in order to establish their identity or dissimilarity, thus:



Isobutylic alcohol.



Supposed 5th butylic alcohol.

In like manner it can be proved that the above four formulæ represent the only possible forms of butylic alcohol, unless the separate bonds of carbon possess different values, in which case the number of possible isomers must be much more numerous.

A secondary monacid alcohol of the $\text{C}_n\text{H}_{2n+1}\text{Ho}$ series is one which, on oxidation, loses two atoms of hydrogen, but does not at the same time take up oxygen in their place, a ketone instead of an acid being produced. The above formula for isopropylic alcohol $\left(\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CMeHHo} \end{array} \right. \right)$ indicates this peculiarity by showing that the atom of carbon which is united with hydroxyl, instead of being also combined with two atoms of hydrogen, as in normal propylic alcohol, is united with an atom of methyl, and, consequently, with only one atom of hydrogen; it is therefore evidently impossible for the group CMeHHo to pass, without loss of carbon, into oxatyl (COHo) by oxidation.

A tertiary monacid alcohol of the $\text{C}_n\text{H}_{2n+1}\text{Ho}$ series is one which, on oxidation, forms neither an acid nor a ketone containing the same number of atoms of carbon as the original alcohol. The molecule of a tertiary alcohol breaks up on oxidation, so as to give two products, each containing less carbon than the body from which it is derived.

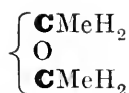
Diacid Alcohols or Glycols.



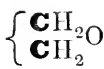
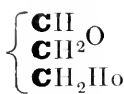
Ethylenic glycol.



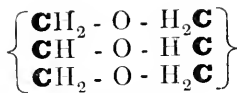
Propylenic glycol

Ethers.

Ethylic ether.

Ethylenic
oxide.

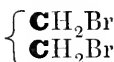
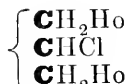
Glycide.



Glycylic ether.

Haloid Ethers.

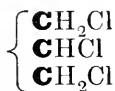
Ethylic iodide.

Ethylenic
bromide.Ethylenic
chlorhydrate.

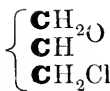
Chlorhydrin.



Dichlorhydrin.



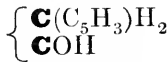
Trichlorhydrin.



Epichlorhydrin.

Aldehydes.

Acetic aldehyde.



Benzoic aldehyde.



Glyoxal.

Monobasic Acids.

I. ACETIC SERIES.

Normal.



Acetic.



Propionic.

Secondary.



Dimethacetic.

Tertiary.



Trimethacetic.

II. LACTIC SERIES.

For the application of this notation to the eight families of these acids, see "Philosophical Transactions," vol. 156, page 345.

III. GLYOXYLIC SERIES.

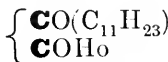
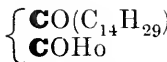
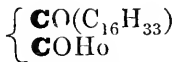


Glyoxylic acid.

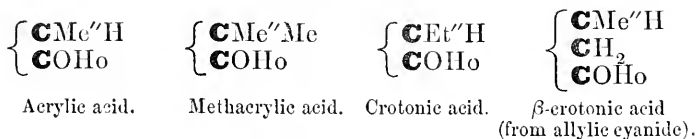


Glyceric acid.

IV. PYRUVIC SERIES.

Glyoxalic
acid.Pyruvic
acid.Convolvulinoleic
acid.Jalapinoletic
acid.Ricinoleic.
acid.

V. ACRYLIC SERIES.

*Dibasic Acids.*

I. SUCCINIC OR ACETOÏD SERIES.



II. MALIC OR LACTOÏD SERIES.



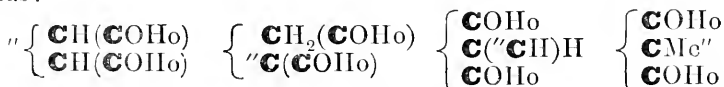
III. TARTARIC OR GLYOXYLOÏD SERIES.



IV. FUNARIC OR ACRYLOÏD SERIES.

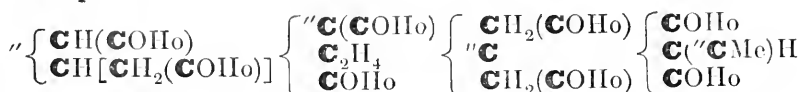
In this series there are three isomeric acids containing four atoms of carbon, viz.: the fumaric, maleic, and isomaleic acids, and the same number containing five carbon atoms, viz., itaconic acid, citraconic acid, and mesaconic acid.

Rational notation allows us to predict the existence of a fourth acid belonging to the four-carbon group. The following are the only four possible formulæ for these acids, but we are not yet able to assign its own particular formula to each of the three known acids:—



For the five-carbon group of these acids there are no less than eleven possible formulæ, consequently we may safely predict a great addition to the number of known isomeric acids belonging

to this group. The following four formulæ may suffice as examples:—



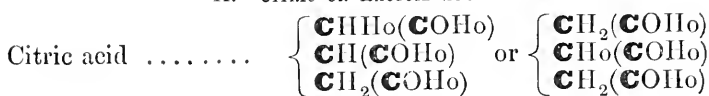
In these formulæ the symbol "C signifies carbon with two of its bonds latent, as in carbonic oxide "CO.

Tribasic Acids.

I. TRICARBALLYLIC OR ACETOÏD SERIES.



II. CITRIC OR LACTOÏD SERIES.



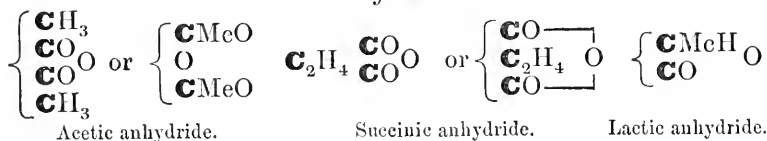
III. DESOXALIC SERIES.



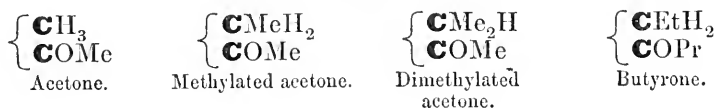
IV. ACONITIC OR ACRYLOÏD SERIES.



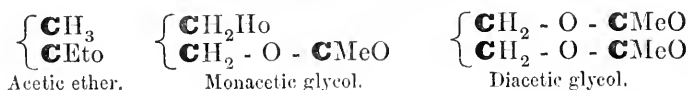
Anhydrides.

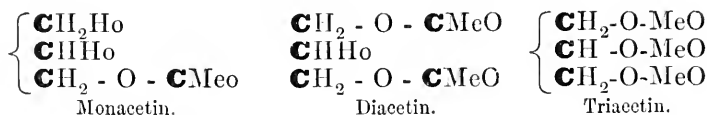
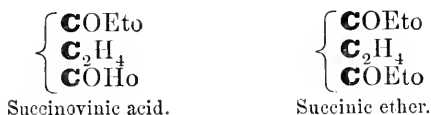


Ketones.



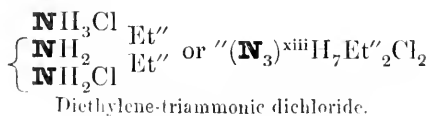
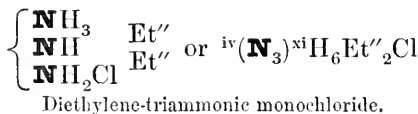
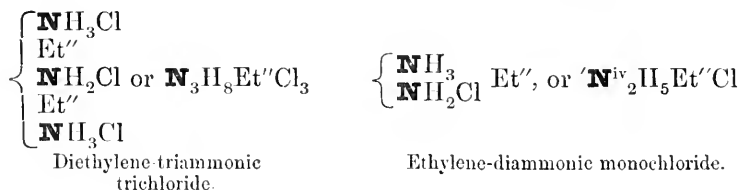
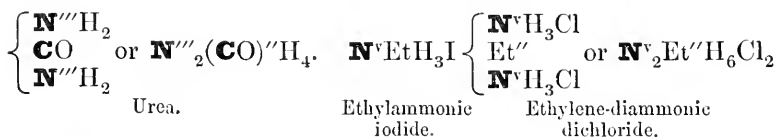
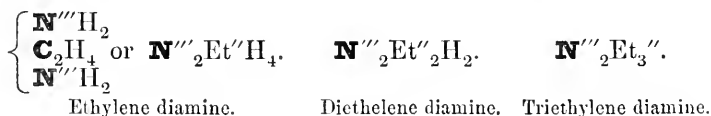
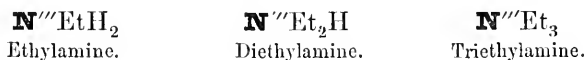
Ethereal Salts.

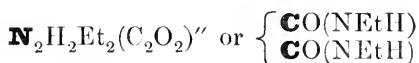
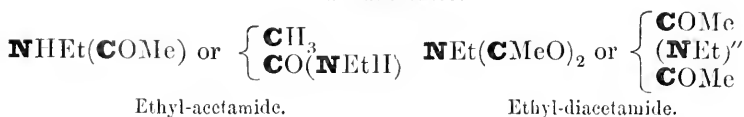




Organic Bases and their Compounds.

In the following examples of the notation of these bodies I have inserted atomicity marks, in order to distinguish triad from pentad nitrogen; these marks are, however, unnecessary except in such cases as that of diethylene-triammonic monochloride.



Alkalamides.

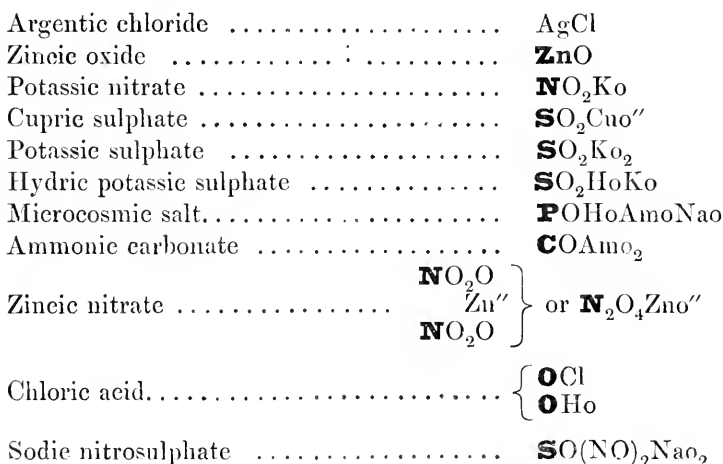
Diethyloxamide.

Amides.

In these, as well as in the nitrogenous compounds above formulated, either carbon or nitrogen may be employed as the grouping element; in the case of the organic bases, there are certain advantages in thus employing nitrogen, whilst, in the case of amides, carbon lends itself better for this purpose; as the following instances will sufficiently exemplify:—



I have already mentioned that this constitutional notation is equally applicable to inorganic compounds; the following examples may serve to illustrate its application in this direction:—



Sulphuric acid	SO_2Ho_2
Sulphosulphuric acid (<i>Hyposulphurous acid</i>)	$\text{S}''\text{OHo}_2$
Nordhausen sulphuric acid	$\left\{ \begin{array}{l} \text{SO}_2\text{Ho} \\ \text{O} \\ \text{SO}_2\text{Ho} \end{array} \right.$
Dithionic acid (<i>Hyposulphuric acid</i>) ..	$\left\{ \begin{array}{l} \text{SO}_2\text{Ho} \\ \text{SO}_2\text{Ho} \end{array} \right.$ or $\text{S}^{\text{v}}_2\text{O}_4\text{Ho}_2$
Trithionic acid (<i>Sulphodithionic acid</i>)....	$\left\{ \begin{array}{l} \text{SO}_2\text{Ho} \\ \text{S}'' \\ \text{SO}_2\text{Ho} \end{array} \right.$
White crystalline compound from sulphuric acid chambers.....	$\left\{ \begin{array}{l} \text{SO}_2(\text{N}^{\text{v}}\text{O}_2) \\ \text{O} \\ \text{SO}_2(\text{N}^{\text{v}}\text{O}_2) \end{array} \right.$
Anhydrous sodic bisulphate (<i>Disodic disulphate</i>)	$\left\{ \begin{array}{l} \text{SO}_2\text{NaO} \\ \text{O} \\ \text{SO}_2\text{NaO} \end{array} \right.$
Dizincic sulphate	SOZno''_2
Trizincic sulphate	SZno''_3
Crystallised gypsum (<i>Tetrahydric calcic sulphate</i>)	$\left\{ \begin{array}{l} \text{SHo}_4\text{Cao}'' \end{array} \right.$
Gypsum dried at 100° C (<i>Dihydric calcic sulphate</i>) ..	$\left\{ \begin{array}{l} \text{SOHo}_2\text{Cao}'' \end{array} \right.$
Gypsum dried at 260° C (<i>Calcic sulphate</i>)	$\text{SO}_2\text{Cao}''$
Zircon	SiZro''_2
Diopside	$\left\{ \begin{array}{l} \text{SiO} \\ \text{SiO} \end{array} \right.$ $\text{Cao}''\text{Mgo}''$
Steatite	$\text{Si}_4\text{O}_5\text{Mgo}''_3$
Meerschaum (<i>Tetrahydric dimagnesian trisilicate</i>)	$\left\{ \begin{array}{l} \text{SiHoMgo}'' \\ \text{O} \\ \text{SiHo}_2 \\ \text{O} \\ \text{SiHoMgo}'' \end{array} \right.$
Anorthite (<i>Aluminic calcic disilicate</i>)	$\text{Si}_2(\text{Al}_2''' \text{O}_6)^{\text{vi}}\text{Cao}''$
Felspar (<i>Dipotassic aluminic hexasilicate</i>)	$\text{Si}_6\text{O}_8(\text{Al}_2''' \text{O}_6)^{\text{vi}}\text{Ko}_2$
Metastannic acid (dried at 100° C)	$\left\{ \begin{array}{l} \text{SnHo}_3 \\ \text{O} \\ \text{SnHo}_2 \\ \text{O} \\ \text{SnO} \\ \text{O} \\ \text{SnHo}_2 \\ \text{O} \\ \text{SnHo}_3 \end{array} \right.$

Ditanic dinitride.....	$\left\{ \begin{array}{l} \mathbf{TiN}''' \\ \mathbf{TiN}''' \end{array} \right.$
Phosphoric acid	\mathbf{POHo}_3
Metaphosphoric acid	$\mathbf{PO}_2\mathbf{Ho}$
Pyrophosphoric acid	$\mathbf{P}_2\mathbf{O}_3\mathbf{Ho}_4$
Hexasodic tetrphosphate (Fleitmann & Henneberg)	$\mathbf{P}_4\mathbf{O}_7\mathbf{NaO}_6$
Dodecasodic decaphosphate (Fleitmann & Henneberg).....	$\mathbf{P}_{10}\mathbf{O}_{19}\mathbf{NaO}_{12}$
Apatite (<i>Francolite</i>)	$\mathbf{P}_3\mathbf{O}_3\mathbf{Cao}''_4 \left(\begin{array}{c} \mathbf{O} \\ \mathbf{F} \end{array} \mathbf{Ca}'' \right)$
Pyromorphite	$\mathbf{P}_3\mathbf{O}_3\mathbf{Pbo}''_4 \left(\begin{array}{c} \mathbf{O} \\ \mathbf{Cl} \end{array} \mathbf{Pb}'' \right)$
Trisulphoplumbic sulphantimonite (<i>Boulangerite</i>)	$\mathbf{Sb}_2\mathbf{Pbs}''_3$
Sulphargentic metasulphantimonite (<i>Miargyrite</i>)	$\mathbf{SbS}''\mathbf{Ags}$
Bismuthous nitrate dihydrate (<i>Basic bismuthous nitrate</i>)	$\mathbf{NO}_2(\mathbf{Bi}'''\mathbf{OHo}_2)$
Sulpho-plumbicsulphobismuthite (<i>Kobellite</i>)	$\mathbf{Bi}_2\mathbf{Pbs}''_3$
Bleaching powder (<i>Calcic chloro-hypochlorite</i>)	$\mathbf{Ca}(\mathbf{OCl})\mathbf{Cl}$
Dolomite	$\left\{ \begin{array}{l} \mathbf{CO} \\ \mathbf{CO} \end{array} \mathbf{Cao}''\mathbf{Mgo}'' \right.$
Guanite (<i>Diammonic dimagnesian diposphate</i>)	$\left\{ \begin{array}{l} \mathbf{POAmo} \\ \mathbf{POAmo} \end{array} \mathbf{Mgo}''_2 \right.$
Dihydric pentazincic dicarbonate tetrahydrate (<i>Basic zincic carbonate</i>)	$\left\{ \begin{array}{l} \mathbf{CHIo}(\mathbf{OZn}''\mathbf{Ho})_2 \\ \mathbf{Zno}'' \\ \mathbf{CHIo}(\mathbf{OZn}''\mathbf{Ho})_2 \end{array} \right.$
Mercurioso-diammonic dichloride	$\left\{ \begin{array}{l} \mathbf{NH}_3\mathbf{ClHg} \\ \mathbf{NH}_3\mathbf{ClHg} \end{array} \right.$
White precipitate (<i>Mercuric-ammonic chloride</i>).....	$\mathbf{NH}_2\mathbf{Hg}''\mathbf{Cl}$
Blue malachite	$\left\{ \begin{array}{l} \mathbf{CHIoCu}'' \\ \mathbf{Cu}'' \\ \mathbf{CHIoCu}'' \end{array} \right.$
Malachite	$\mathbf{CO}(\mathbf{OCu}''\mathbf{Ho})_2$
Diopase	$\mathbf{SiOHo}(\mathbf{OCu}''\mathbf{Ho})$
Gibbsite	$\left\{ \begin{array}{l} \mathbf{AlHo}_3 \\ \mathbf{AlHo}_3 \end{array} \right.$
Diaspore	$\mathbf{Al}'''\mathbf{O}_2\mathbf{Ho}_2 \text{ or } \left\{ \begin{array}{l} \mathbf{AlOHo} \\ \mathbf{AlOHo} \end{array} \right.$
Spinelle	$\mathbf{Al}'''\mathbf{O}_2\mathbf{Mgo}'' \text{ or } \left\{ \begin{array}{l} \mathbf{Al} \\ \mathbf{Al} \end{array} \mathbf{O}_2\mathbf{Mgo}'' \right.$

Potash alum	$\left\{ \begin{array}{l} \text{SO}_2\text{Ko} \\ \text{SO}_2\text{—} \\ \text{SO}_2\text{—} \\ \text{SO}_2\text{Ko} \end{array} \right\} (\text{Al}'''_2\text{O}_6)^{\text{vi}}, 24\text{OH}_2$
Porcelain clay	$\left\{ \begin{array}{l} \text{SiHo} \\ \text{O —} \\ \text{SiHo} \end{array} \right\} (\text{Al}'''_2\text{O}_4\text{Ho}_2)^{\text{iv}}$
Porcelain clay of Passan	$\left\{ \begin{array}{l} \text{SiHo}_2 \\ \text{SiHo}_2 \end{array} \right\} (\text{Al}'''_2\text{O}_4\text{Ho}_2)^{\text{iv}}$
Platinoso-diammonic dichloride (<i>Magnus's green salt</i>)	$\left\{ \begin{array}{l} \text{NH}_3\text{Cl} \\ \text{Pt}'' \\ \text{NH}_3\text{Cl} \end{array} \right\}$
Lanarkite (<i>Diplumbic sulphate carbonate</i>) . .	$\left\{ \begin{array}{l} \text{CO} \\ \text{SO}_2 \end{array} \right\} \text{Pbo}''_2$
Potassic chromate	CrO_2Ko_2
Dipotassic dichromate (<i>Bichromate of potash</i>)	$\left\{ \begin{array}{l} \text{CrO}_2\text{Ko} \\ \text{O} \\ \text{CrO}_2\text{Ko} \end{array} \right\}$
Dipotassic trichromate (<i>Terchromate of potash</i>)	$\left\{ \begin{array}{l} \text{CrO}_2\text{Ko} \\ \text{O} \\ \text{CrO}_2 \\ \text{O} \\ \text{CrO}_2\text{Ko} \end{array} \right\}$
Manganite	$\left\{ \begin{array}{l} \text{MnOHo} \\ \text{MnOHo} \end{array} \right\}$
Varvicite	$\left\{ \begin{array}{l} \text{MnO — O} \\ \text{Mno}'' \\ \text{MnO — O} \end{array} \right\} (\text{Mn}^{\text{iv}}\text{Ho}_2)''$
Brown hæmatite	$\left\{ \begin{array}{l} \text{FeOHo} \\ \text{FeHo}_2 \\ \text{O} \\ \text{FeHo}_2 \\ \text{FeOHo} \end{array} \right\}$
Needle iron ore	$\left\{ \begin{array}{l} \text{FeOHo} \\ \text{FeOHo} \end{array} \right\}$

In conclusion I append a table of elements classified according to their atomicities as employed in this plan of notation.

Monads.	Dyads.	Triads.	Tetrads.	Pentads.	Hexads.
1st Section.	1st Section.	1st Section.	1st Section.	1st Section.	1st Section.
Hydrogen.	Oxygen.	Boron.	Carbon. Silicon. Tin.	Nitrogen. Phosphorus. Arsenic. Antimony. Bismuth.	Sulphur. Selenium. Tellurium.
2nd Section.	2nd Section.	2nd Section.	Titanium.		
Fluorine. Chlorine. Bromine. Iodine.	Barium. Strontium. Calcium. Magnesium. Zinc.	Gold.	2nd Section. Thorium. Niobium. Tantalum. Zirconium. Aluminium.		2nd Section. Tungsten. Vanadium. Molybdenum.
3rd Section.	3rd Section.		3rd Section. Platinum. Palladium.		3rd Section. Osmium. Iridium. Ruthenium. Rhodium.
Cæsium. Rubidium. Potassium. Sodium. Lithium.	Didymium. Lanthanum. Yttrium. Glucinum.		4th Section. Lead.		4th Section. Chromium. Manganese. Iron. Cobalt. Nickel. Uranium. Cerium.
4th Section.	4th Section.				
Thallium. Silver.	Cadmium. Mercury. Copper.				

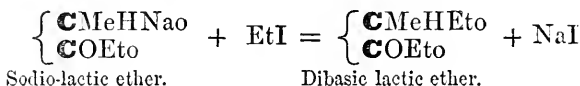
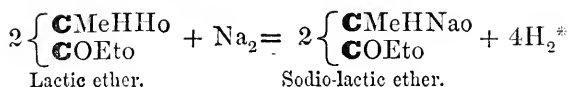
XL.—Synthetical Researches on Ethers.—No. 1. Synthesis of Ethers from Acetic Ether.

By E. FRANKLAND, F.R.S., and B. F. DUPPA, Esq.

(From the Philosophical Transactions, Vol. clvi, p. 37.)

IN his researches upon lactic acid Wurtz* contends with considerable force for the dibasicity of this acid, supporting his view by the transformation of monobasic into dibasic lactic ether by the consecutive action of sodium and ethylic iodide, as expressed in the following equations:

* Ann. Ch. Phys. lix, 161.



During the prosecution of our researches upon acids of the acetic series,† we have obtained several so-called dibasic ethers of this description; but before finally deciding upon the interpretation to be put upon such reactions, it appeared advisable to ascertain the effect of the same reagents upon a well-defined monobasic ether. For this purpose acetic ether was selected, and was treated, first, with sodium, and then with ethylic, methylic, and amylic iodides respectively. The results, although not strictly analogous with those obtained under similar circumstances with ethers of the lactic series, are highly remarkable. We have already briefly referred to them in a note presented to the Royal Society in April 1865.‡

Action of Sodium and Ethylic Iodide upon Acetic Ether.

The acetic ether used for this and the succeeding reactions was made as follows:—

6,000 grms. of previously dried and fused sodic acetate was broken into small pieces and placed in a copper still immersed in cold water. Over this was gradually poured 12,600 grms. of a mixture of 3,600 grms. alcohol§ of 97 per cent., and 9,000 grms. concentrated sulphuric acid, taking care that the temperature did not rise high enough to distil off any of the product. The success of the operation depends greatly upon the mode of mixing the alcohol and sulphuric acid, which ought to be performed as follows. The sulphuric acid being placed in a deep stoneware vessel of sufficient capacity, the alcohol is conducted to the bottom of it by means of a piece of narrow glass tube, connected by a caoutchouc

* For an exposition of the system of notation adopted in this memoir see the preceding paper.

† Proceedings of the Royal Society, xii, 396; xiii, 110; xiv, 17, 79, 83, 191, and 197.

‡ Ibid. xiv, 198.

§ Methylated spirit may be used for this purpose.

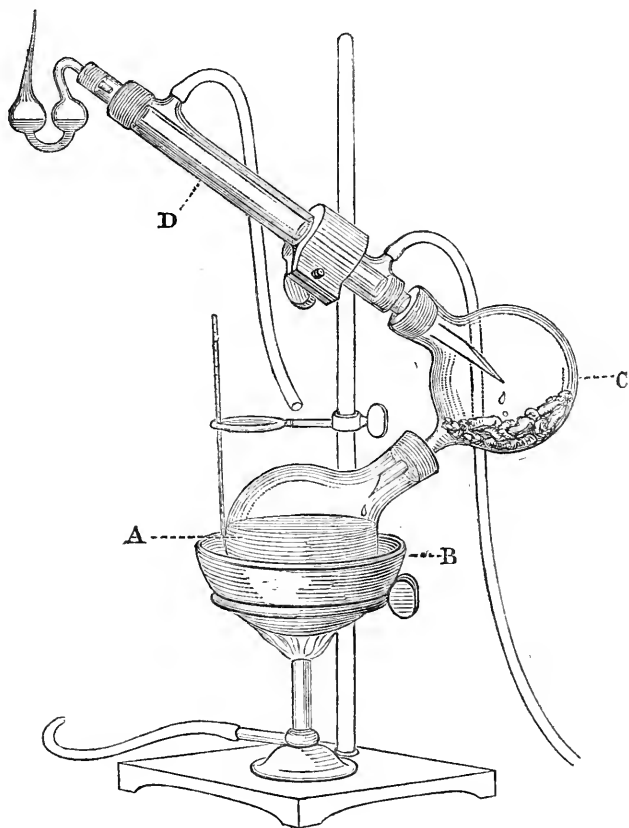
tube with a convenient reservoir standing at a considerable elevation. The glass tube is used as an agitator during the continuance of the flow of the alcohol. In this way there is obtained, without loss of alcohol, a high temperature which greatly favours the formation of sulphovinic acid. This mixture must be allowed to stand, carefully covered up, for twenty-four hours before use.

It is also advisable to make the admixture of sulphovinic acid and sodic acetate at least twelve hours before the distillation is commenced. The latter operation can then be performed over a naked fire or gas-flame, and continued till water alone passes over. In this way there was obtained 6,000 grms. of an acetic ether absolutely free from alcohol, and which, without previous washing only needs one rectification from fused and powdered calcic chloride to fit it for the action of sodium. A determination of its vapour-density gave the number 2.9. Pure acetic ether requires 3.04.

When acetic ether thus prepared is placed in contact with sodium it becomes hot, and a considerable quantity of gas is evolved, which, after being passed first through alcohol and then through water, burns with a non-luminous flame, and the products of combustion do not produce the slightest turbidity on agitation with baryta-water. In fact the gas is pure hydrogen. When the action is complete, the liquid solidifies on cooling to a mass resembling yellow beeswax. By putting the sodium into the acetic ether as just described, it is difficult to conduct the operation to completion, owing to the liquid gradually assuming such a thick and pasty condition as to prevent the further action of the sodium. We therefore adopted the following modification, which enabled us to push the reaction almost to its extreme limit.

A (fig. 1) is a flask containing the acetic ether, and standing in an oil-bath, B. The neck of the flask was closed with a caoutchouc cork, through which passed the beak of the quilled receiver C, containing the sodium cut up into pieces about 1 inch square and $\frac{1}{4}$ inch thick. Into the wide neck of this receiver was inserted an inverted Liebig's condenser, D, which projected sufficiently into the vessel to allow the condensed liquid to drip back upon the sodium. Heat being applied to the oil-bath, the acetic ether soon began to boil, and by its condensation in C and D not only kept the surface of the sodium constantly moist with fresh portions of acetic ether, but also dissolved off the solid sodium-compound as fast as formed. As the operation progressed it was found

necessary to raise the temperature of the oil-bath, so as to cause the continuous distillation of the remaining acetic ether, which acquired a higher boiling-point as the proportion of sodium compound dissolved in it increased; but the temperature ought not to be allowed to rise above 130°C . When the acetic ether ceases to distil at this temperature, the proportion of sodium dissolved is not much below one atom for each atomic proportion of acetic



ether employed, and it was not found advantageous to push the reaction further. The contents of the flask were now submitted to the action of ethylic iodide, for which purpose they were transferred whilst still liquid to an iron digester, and mixed with a quantity of ethylic iodide equivalent to the amount of sodium

dissolved. The digester was then exposed to a temperature of 100°C . in a steam-bath for some hours, and after being allowed to cool, water in considerable bulk was introduced, and the whole submitted to distillation in an oil-bath. There first came over a large quantity of ethylic ether mixed with some acetic ether that had escaped decomposition. As the temperature in the interior of the digester rose above 100° , the distillate began to separate into an aqueous and an ethereal portion, and further quantities of water were repeatedly added until no more ethereal liquid distilled. The ethereal, separated from the aqueous portion, presented the appearance of a light straw-coloured oil, possessing a pleasant and fragrant colour. It was washed with water, then dried over calcic chloride, and submitted to fractional distillation, by which traces of alcohol, acetic ether, and ethylic iodide were effectually removed from the other products, which now boiled between 120° and 265° . It will be most convenient to describe the constituents of this complex liquid under two distinct heads, viz. :—

1st. Products depending upon the duplication of the molecule of acetic ether.

2nd. Products derived from the substitution by the alcohol-radicals of hydrogen in the methyl of acetic ether.

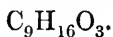
In order successfully to separate the two products from each other, and especially to disentangle their constituent compounds, it is absolutely necessary to operate upon large quantities of material. But if this be done, there is obtained a considerable quantity of the products of the first division boiling between 204° and 208°C ., whilst the products of the second division boil considerably below these temperatures.

α. Examination of the products depending upon the duplication of the molecule of acetic ether.

Submitted to analysis, this liquid gave the following numbers :—

- I. ·3920 grm. gave ·9010 grm. carbonic anhydride and ·3291 grm. water.
- II. ·2772 grm. gave ·6347 grm. carbonic anhydride and ·2338 grm. water.

These numbers agree very closely with the formula



as the following comparison shows:—

Calculated.		Found.		
		I.	II.	Mean.
C ₉	108 62·79	62·75	62·45	62·60
H ₁₆	16 9·22	9·33	9·37	9·35
O ₃	48 27·99			
	<hr/> 172 100·00			

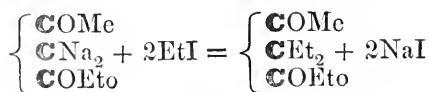
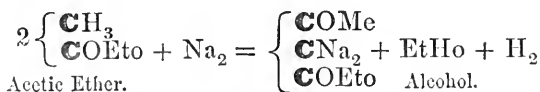
In addition to this very close correspondence between the experimental and calculated values, a vapour-density determination gave the number 6·001, the above formula requiring 5·94; nevertheless the body in question is not a single substance, for after being boiled for several hours with aqueous potash, its boiling-point rose to between 210° and 212°, and on being again submitted to analysis it gave results required by the formula



- I. ·2626 grm. gave ·6184 grm. carbonic anhydride and ·2308 grm. water.
 II. ·3339 grm. gave ·7896 grm. carbonic anhydride and ·2924 grm. water.

Calculated.		Found.		
		I.	II.	Mean.
C ₁₀	120 64·52	64·22	64·49	64·36
H ₁₈	18 9·68	9·77	9·73	9·75
O ₃	48 25·80			
	<hr/> 186 100·00			

From considerations which are fully entered into below, we propose for this body the name *ethylic diethacetone carbonate*. The formation of this compound is explained in the following equations:—



Ethylic diethacetone
carbonate.

Ethylie diethacetone carbonate is a colourless and somewhat oily liquid, possessing a fragrant odour and a pungent taste. It is insoluble in water, but miscible in all proportions with alcohol or ether. Its specific gravity is $\cdot 9738$ at 20° C. It boils between 210° and 212° , and distils unchanged. The density of its vapour was calculated from the following numbers to be $6\cdot 59$.

Weight of liquid	$\cdot 1978$ gm.
Observed volume of vapour . . .	$46\cdot 01$ cub. centims.
Temperature of bath	232° C.
Height of barometer	767 millims.
Difference of heights of mercury inside and outside tube	$76\cdot 5$ millims.
Height of spermaceti column re- duced to millims. of mercury	$15\cdot 1$ millims.

The above formula, corresponding to two volumes, requires the number $6\cdot 43$.

Boiling aqueous solutions of potash and soda have scarcely any action on ethylie diethacetone carbonate, but baryta-water and lime-water decompose it with great facility, as do also boiling alcoholic solutions of potash and soda. In all these cases a carbonate of the base is precipitated, whilst alcohol and a light ethereal liquid are produced.

This liquid, freed from alcohol by repeated washing with salt and water, boiled, after drying over calcic chloride, between $137^{\circ}\cdot 5$ and 139° C. Submitted to analysis, it yielded the following results:—

$\cdot 2075$ gm. gave $\cdot 5591$ gm. carbonic anhydride and $\cdot 2313$ gm. water.

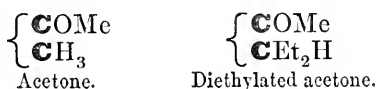
These numbers agree with the formula



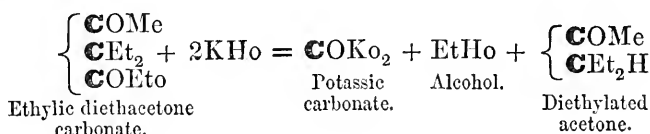
as seen from the following comparison :

	Calculated.		Found.
C_7	84	$73\cdot 68$	$73\cdot 52$
H_{14}	14	$12\cdot 28$	$12\cdot 38$
O	16	$14\cdot 04$	
	<hr/>	<hr/>	
	114	100·00	

From the mode of its formation, and its analogy with other similar bodies described below, this ethereal liquid must be regarded as a ketone, and we propose for it the name *diethylated acetone*. Its rational formula and its relations to acetone may be thus expressed :



Diethylated acetone is produced from ethylic diethacetone carbonate by the action of alcoholic potash according to the following equation :—

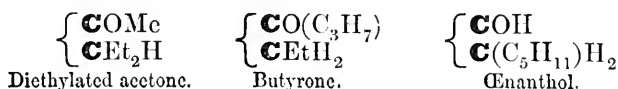


Diethylated acetone is a colourless, transparent, and mobile liquid, possessing a penetrating odour of camphor, and the burning and bitter after-taste of the same substance. It is very slightly soluble in water, but miscible in all proportions with alcohol or ether. Its specific gravity is .8171 at 22° C. It boils at 137°·5 to 139° C. A determination of its vapour-density by Gay Lussac's method gave the following data :—

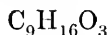
Weight of diethylated acetone.	•1930 grm.
Observed volume of vapour . . .	62·0 cub. centims.
Temperature of bath	161° C.
Height of barometer	773 millims.
Difference of heights of mercury inside and outside tube . . .	39·5 millims.
Height of spermaceti column re- duced to millims. of mercury	15·7 millims.

From these numbers the density was calculated to be 3·86 ; the formula $\text{C}_7\text{H}_{14}\text{O}$ requires the number 3·93. Diethylated acetone does not oxidize in the air, neither does it reduce ammoniacal solution of argentic nitrate when boiled with it. Mixed with concentrated solution of hydric sodic sulphite, it forms an oily compound which scarcely exhibits signs of crystallisation at 0° C. It suffers no alteration by prolonged boiling with alcoholic potash.

It is isomeric with butyrene, with a ketone obtained by Fittig* in the distillation of a mixture of valeraldehyde and quicklime, and with cœnanthol. From the first two it is distinguished by its lower boiling-point (138°), butyrene boiling at 144° C., and Fittig's ketone at 161° to 164° , and from the third by its different properties, which are essentially those of a ketone, and not of an aldehyde. The difference in structure of three of these bodies may be expressed with considerable certainty by the following formulæ:—

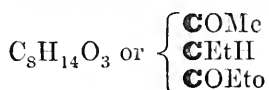


We have mentioned above that ethylic diethacetone carbonate is freed from another body with which it is associated, by long ebullition with aqueous potash. A large quantity of potassic carbonate is formed in this reaction, and there is at the same time a volatile body of a ketonic character set free. This led us to suspect the presence in the original mixture of a lower homologue formed by the action of only one atom of sodium upon two atoms of acetic ether—a suspicion supported by the composition of the mixture as shown by the analyses given at page 399, which indicate the formula



that would be deduced from the analysis of equal weights of ethylic diethacetone carbonate ($\text{C}_{10}\text{H}_{18}\text{O}_3$), and its lower homologue, ethylic ethacetone carbonate ($\text{C}_8\text{H}_{14}\text{O}_3$). Further investigation of the mixture before boiling with aqueous potash completely confirmed this surmise; for by careful fractional distillation we succeeded in separating two liquids of constant boiling-point, one of which was ethylic diethacetone carbonate, and the other *ethylic ethacetone carbonate*. The latter yielded on analysis the following numbers:—2411 grm. gave 5387 grm. carbonic anhydride and 1944 grm. water.

These numbers correspond well with the formula

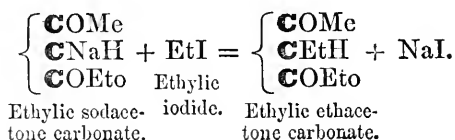
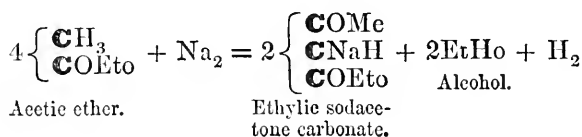


as is seen from the subjoined comparison :

* Ann. Ch. Pharm. cxvii, 68.

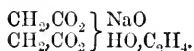
	Calculated.		Found.
C ₈	96	60·76	60·94
H ₁₄	14	8·86	8·96
O ₃	48	30·38	
	<hr/>	<hr/>	
	158	100·00	

The production of ethylic ethacetone carbonate by the action of sodium and ethylic iodide upon acetic ether is explained in the two following equations:*



Ethylic ethacetone carbonate is a colourless and transparent liquid, possessing a very fragrant odour and an aromatic taste. It is nearly insoluble in water, but miscible in all proportions with alcohol and ether. Its density in the liquid condition is ·9834 at 16° C. It boils at 195° C., and distils without decomposition. A determination of its vapour-density gave the following data:—

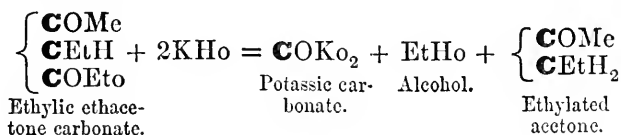
* Whilst engaged in these experiments we became aware, through the “Jahresbericht der Chemie,” that this compound, and the corresponding one made with methylic iodide mentioned below, had already been studied by Geuther, who also obtained ethylic sodacetone carbonate, which he analyzed and designated by the name *Di-methylene-carbon-ethylene-sodic ether*, assigning to it the formula (C=12, O=8),



From this body he produced ethylic ethacetone carbonate (*Di-methylene-carbon-ethylene ether*) by the action of ethylic iodide, and also *ethylic methacetone carbonate* (*Di-methylene-carbon-methylene ether*) by the action of methylic iodide. Our analytical results and observations of the physical properties of these two bodies agree completely with those assigned to them by Geuther, whose isolation of the sodium-compound, attended as it is with great difficulties, serves to impart a completeness to the reaction which it would otherwise have lacked.

Weight of ethylic-ethacetone carbonate ..	·1993 grm.
Observed volume of vapour.....	54·09 cub. centims.
Height of barometer.....	763·5 millims.
Difference of heights of mercury inside and outside tube	76·0 millims.
Height of spermaceti column reduced to mil- lims. of mercury	15·7 millims.

From these numbers the specific gravity was calculated to be 5·36; theory requires 5·45. Ethylic ethacetone carbonate, unlike ethylic-diethacetone carbonate, and in opposition to Geuther's statement, is readily attacked by boiling aqueous solutions of potash and soda, yielding carbonates of these bases, alcohol, and *ethylated acetone* according to the following equation:—



Ethylic ethacetone carbonate is still more readily decomposed by aqueous solution of baryta or by alcoholic potash; in both cases ethylated acetone and a carbonate of the base are produced.

Ethylated acetone may be freed from alcohol by repeated washing with salt and water, but it is best obtained in a state of absolute purity by combination with, and subsequent separation from hydric sodic sulphite. Ethylated acetone thus purified and rectified from quicklime, gave on analysis the following numbers:—

·1483 grm. gave ·3799 grm. carbonic anhydride and ·1575 grm. water.

This result agrees well with the formula



as seen from the following comparison of experimental with theoretical percentage numbers:—

	Calculated.		Found.
	⎵		
C ₅	60	69·77	69·86
H ₁₀	10	11·63	11·80
O.....	16	18·60	
	86	100·00	

The relations of ethylated acetone to acetone and diethylated acetone are seen in the following formulæ:—



Ethylated acetone is a colourless, transparent and very mobile liquid, possessing a powerful and pleasant odour, in which that of camphor is slightly perceptible. Its specific gravity is $\cdot 8132$ at 13°C ., and $\cdot 8046$ at 22°C . It boils steadily at 101° (barom. 760 millims.), and its vapour has the density $2\cdot 951$, as calculated from the following data, theory requiring $2\cdot 971$.

Weight of ethylated acetone	$\cdot 1368$ gm.
Observed volume of vapour.....	$55\cdot 64$ cub. centims.
Temperature of bath	124°C .
Height of barometer	773 millims.
Difference of heights of mercury inside and outside tube	80 millims.
Height of spermaceti column reduced to millims. of mercury.	$15\cdot 7$ millims.

Ethylated acetone neither absorbs oxygen from the air, nor reduces ammoniacal solutions of silver. It yields with concentrated solution of hydric sodic sulphite a compound in large and brilliant crystals, which are quite permanent in the air, and which at once distinguish it from diethylated acetone, the latter producing under the same circumstances an oily compound. Ethylated acetone is not altered by prolonged ebullition with alcoholic potash. Its relations to numerous isomers are described below.

β . Examination of the products derived from the substitution of ethyl for hydrogen in the methyl of acetic ether.

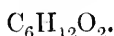
This portion of the original product derived from the action of sodium and ethylic iodide upon acetic ether, and which boiled considerably below the portion α , was submitted to repeated rectifications, and was thus resolved to a great extent into two ethereal liquids, one of them boiling between 118° and 122° , and the other between 150° and 157°C . On treating these liquids with boiling baryta-water for several hours in order to remove traces of ethylic diethacetone carbonate and ethylic ethacetone carbonate, the

point of ebullition of the first was rendered quite constant at 119° C., and that of the second at 151° C.

Submitted to analysis, the first of these liquids yielded the following results:—

- I. 1716 grm. gave 3922 grm. carbonic anhydride and 1626 grm. water.
 II. 2190 grm. gave 5007 grm. carbonic anhydride and 2063 grm. water.

These numbers coincide closely with those calculated from the formula

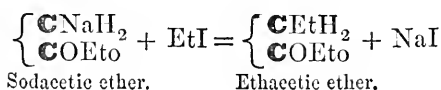
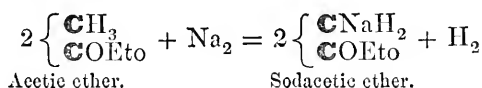


	Calculated.		Found.		Mean.
			I.	II.	
C ₆	72	62·07	62·33	62·35	62·34
H ₁₂	12	10·35	10·53	10·47	10·50
O ₂	32	27·58			
	<hr/>	<hr/>			
	116	100·00			

The formula and habits of this compound show it to be *ethacetic ether* :



Ethacetic ether is produced from acetic ether by the following reactions:—



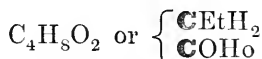
Ethacetic ether possesses all the properties of butyric ether. It is colourless and transparent, and when largely diluted with alcohol possesses the characteristic odour of pine-apples, which is undistinguishable from that of butyric ether under the same circumstances. Its density is 8942 at 0° C., that of butyric ether being, according to Pierre, 9019 at 0°C., numbers which coincide with each other as closely as could be expected. The boiling-point (119° C.) of ethacetic ether also agrees exactly with that of butyric

ether given by the same authority, as does the vapour-density, which was ascertained to be 3·96 from the following data, the theoretical number being 4·04.

Weight of ethacetic ether	·1769	gram.
Observed volume of vapour.	57·24	cub. centims.
Temperature of bath	148°	C.
Height of barometer	763·5	millims.
Difference of height of mercury inside and outside tube	75·7	millims.
Height of spermaceti column reduced to millims. of mercury	15·7	millims.

Ethacetic ether is readily decomposed by boiling alcoholic potash, yielding alcohol and a salt which, when distilled with slight excess of dilute sulphuric acid, gives a powerfully acid oily liquid, tolerably soluble in water, possessing in a high degree the characteristic odour of butyric acid, and boiling fixedly at 161°C. The boiling-point of butyric acid has been variously stated by different observers: Pelouze and Gélis state it to be 164°, whilst Kopp gives it as 157° at 760 millims. pressure.

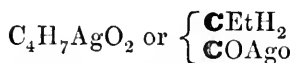
Submitted to analysis, ·2439 grm. *ethacetic acid* gave ·4862 grm. carbonic anhydride and ·2030 grm. water, numbers which correspond with the formula



The following is a comparison of the analytical with the calculated numbers:—

	Calculated.		Found.
C ₄	48	54·54	54·37
H ₈	8	9·00	9·25
O ₂	32	36·37	
	<hr/> 88	<hr/> 100·00	

Boiled with water and argentic carbonate, ethacetic acid yields, after some hours, a crop of beautiful ramiform needle-like crystals, aggregated into large globular masses, which become anhydrous *in vacuo*; both the mother-liquor and crystals have a faint smell of rancid butter. Submitted to analysis, these crystals yielded results agreeing with the formula for argentic ethacetate,



·2738 grm. gave ·2463 grm. carbonic anhydride, ·0889 grm. water, and ·1518 grm. silver.

	Calculated.		Found.
C ₄	48	24·61	24·53
H ₇	7	3·59	3·61
Ag	108	55·38	55·44
O ₂	32	16·42	
	<hr/>	<hr/>	
	195	100·00	

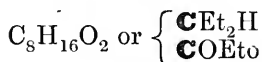
We have been unable to detect any difference between ethacetic acid and butyric acid, and we have stated below our reasons for believing them to be identical.

The second portion of the product β , mentioned above as a liquid boiling at 151° C., was next submitted to analysis.

I. ·2276 grm. gave ·5523 grm. carbonic anhydride, and ·2279 grm. water.

II. ·1839 grm. gave ·4461 grm. carbonic anhydride, and ·1817 grm. water.

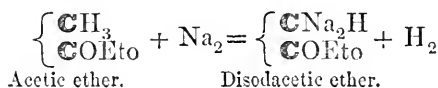
These results correspond with the formula of *diethacetic ether*,

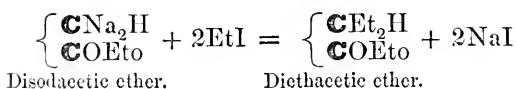


as is seen from the following comparison:—

	Calculated.		Found.	
	<hr/>		I.	II.
C ₈	96	66·66	66·18	66·16
H ₁₆	16	11·11	11·13	11·16
O ₂	32	22·23		
	<hr/>	<hr/>		
	144	100·00		

Diethacetic ether is derived from acetic ether by the following reactions:—





Diethacetic ether is a colourless and transparent liquid of a peculiar and fragrant odour, and a taste somewhat like peppermint. Its specific gravity is $\cdot 8822$ at 0°C . It is insoluble in water, but miscible in all proportions with alcohol and ether. It boils constantly at 151°C ., and its vapour has, theoretically, the density $4\cdot 98$. Experimentally the number $5\cdot 00$ was obtained.

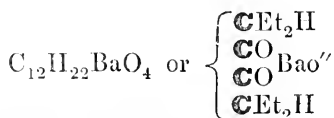
Treated with alcoholic potash, diethacetic ether is readily decomposed, yielding alcohol and potassic diethacetate. By distilling the latter with dilute sulphuric acid, diethacetic acid passes over and floats on the surface of the water which accompanies it. This acid reddens litmus-paper powerfully, is but sparingly soluble in water, and emits a peculiar odour quite different from that of caproic acid, with which diethacetic acid is isomeric. Boiled with water and argentic carbonate, it yields, on filtration and evaporation *in vacuo*, splendid fern-like crystals, which, after pressing between folds of blotting-paper and drying *in vacuo*, with the exclusion of light, are perfectly white, with a satiny lustre; they possess great elasticity, and are remarkably like asbestos. In a strong light they rapidly become brown. Submitted to analysis, it gave numbers agreeing with the formula

$$\text{C}_6\text{H}_{11}\text{AgO}_2 \text{ or } \left\{ \begin{array}{l} \text{CEt}_2\text{H} \\ \text{COAgO} \end{array} \right.$$

	Calculated.		Found.
C ₆	72	32·28	31·86
H ₁₁	11	4·93	5·04
Ag	108	48·43	49·25
O ₂	32	14·36	13·85
	<hr/>	<hr/>	<hr/>
	223	100·00	100·00

Baric diethacetate is very soluble in water, and on evaporation forms a beautifully crystalline mass.

A determination of barium in this salt yielded $38\cdot 05$ per cent.; the formula



requires $37\cdot 33$ per cent. of barium.

Diethacetic acid differs markedly from caproic acid in its odour, as above mentioned, whilst the compounds of the two acids scarcely permit of their being confounded with each other. Thus diethacetic ether differs from caproic ether by 11° in its boiling-point, which is 151° C., the boiling-point of caproic ether being, according to Fehling, 162° . In their specific gravities also the two ethers appreciably differ, caproic ether having a density of $\cdot 882$ at 18° C., whilst the specific gravity of diethacetic ether is $\cdot 8322$ at 0° C. The silver-salts differ widely in their crystalline form, solubility in water, and sensitiveness to the influence of light. Silver caproate crystallizes in large and very thin plates, which are nearly insoluble in water, and but very slightly sensitive to light, whilst silver diethacetate is deposited in frond-like crystals, which are quite as soluble as silver acetate, and become rapidly brown when exposed to light. We therefore conclude that these acids are isomeric and not identical. Theoretical considerations leading to the same conclusion are given below.

Action of Sodium and Methylic Iodide upon Acetic Ether.

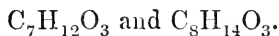
Acetic ether was treated with sodium, as in the corresponding reaction described above; but in the subsequent treatment of the sodium-compound it was not found necessary to expose the mixture of the latter with methylic iodide to heat in a digester. These materials act upon each other with great energy and completeness at a temperature below the boiling-point of methylic iodide. At the conclusion of the sodium-reaction, therefore, the temperature was allowed to fall until the liquid in the flask began to solidify, and the receiver, C (see figure, p. 398), with the residue of sodium being removed, the extremity of the condenser was inserted into the neck of the flask. Methylic iodide in excess was then slowly added by pouring it down the condenser. An energetic action immediately took place, a large quantity of sodic iodide being formed. To complete this reaction, one atom of methylic iodide for each atom of sodium employed was found to be sufficient. The ethereal part of the product in the flask now remained liquid, even after cooling, the sodic iodide subsiding as a dense precipitate. Water was then added, and the contents of the flask submitted to distillation. Water, alcohol, and an oily liquid which floated on the aqueous portion of the distillate, condensed in the receiver. When the oily liquid ceased to come over, the contents of the

retort were slightly acidified with dilute sulphuric acid, more water added, and the distillation continued into a fresh receiver. The acid distillate thus obtained did not contain any formic acid, and consisted chiefly of acetic acid, with traces of other higher acids belonging to the same series.

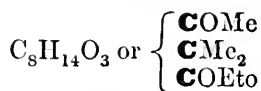
The aqueous portion of the distillate was separated from the oily, and submitted to distillation in an oil-bath. A considerable quantity of a spirituous liquid passed over, which, after rectification from quick-lime, boiled at $78\cdot5^{\circ}$, and consisted of pure alcohol. It yielded on combustion 52·29 per cent. of carbon and 12·98 per cent. of hydrogen. Alcohol requires 52·17 per cent. of carbon and 13·04 per cent. of hydrogen.

The oily portion of the distillate was repeatedly washed with water, dried over calcic chloride, and rectified. It began to boil at 75° , but the thermometer rapidly rose to 183° , between which temperature and 184° nearly the whole of the remaining large portion of liquid came over.

Notwithstanding the constancy of boiling-point of this liquid, numerous analyses showed it to be a mixture, and the numbers obtained were consistent with the assumption that it was composed of two bodies having respectively the formulæ



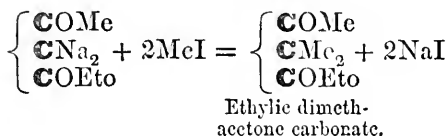
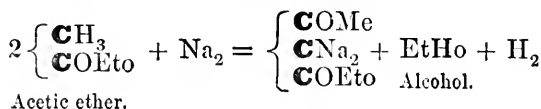
In fact it was evident that the liquid with which we had now to do was the exact counterpart of the one obtained in the corresponding reaction with ethylic iodide described above, and that it consisted of the homologues produced in the ethylic reaction, viz., *ethylic methacetone carbonate* and *ethylic dimethacetone carbonate*. To separate these compounds, whose boiling-points were evidently nearly if not absolutely identical, we availed ourselves of their different behaviour with boiling aqueous potash; ethylic dimethacetone carbonate, like ethylic diethacetone carbonate, being scarcely affected by this treatment, whilst ethylic methacetone carbonate, like its ethylic homologue, is rapidly decomposed. By thus boiling several ounces of the mixed ethers with aqueous potash, a liquid was obtained which, by repeated rectification, was separated into two products, the one boiling at about 80°C ., and the other constantly at 184°C . The latter was submitted to analysis, and yielded results approximating closely to those required by the formula of ethylic dimethacetone carbonate,



as shown by the following comparison :—

Calculated.		Found.							
		I.	II.	III.	IV.	V.	VI.	Mean.	
C ₈ ..	96	60·76	60·45	60·47	60·36	60·26	60·71	60·86	60·52
H ₁₄ ..	14	8·86	8·87	8·88	8·77	9·00	9·11	9·05	8·95
O ₃ ..	48	30·38							
	<hr/>	<hr/>							
	158	100·00							

The production of ethylic dimethacetone carbonate from acetic ether is explained by the following equations :—



Ethylic dimethacetone carbonate is a colourless, slightly oleaginous liquid, possessing a peculiar penetrating, pleasant and aromatic odour, and a sharp burning taste. It is scarcely at all soluble in water, but readily so in alcohol or ether. Its specific gravity is ·9913 at 16° C. It boils constantly at 184°, and distils unchanged. A determination of its vapour-density gave the number 5·36. The above formula, corresponding to two volumes, requires 5·45.

Ethylic dimethacetone carbonate is very slowly acted upon by aqueous solution of potash or soda. A quantity of it was boiled, without any perceptible diminution of its volume, with two separate portions of strong solution of potash for eight or ten hours, an inverted condenser being attached to the flask.

Alcoholic potash in the cold decomposes it very slowly, but when heated to boiling complete decomposition is effected in a very short time. The action is the same as that of baryta-water.

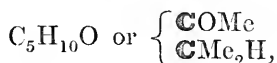
Baryta-water instantly attacks ethylic dimethacetone carbonate

in the cold, baric carbonate being immediately precipitated. At 100° C. the decomposition is complete in a few minutes; and on submitting the mixture to distillation, alcohol and a light ethereal liquid pass over. The latter, repeatedly washed with a saturated solution of common salt to remove alcohol, and dried over quicklime, gave, on analysis, the following numbers:—

- I. 2083 grm. gave 5301 grm. carbonic anhydride and 2220 grm. water.
 II. 2594 grm. gave 6572 grm. carbonic anhydride and 2728 grm. water.

When the mode of its formation is considered, these results show that the body analysed is *dimethylated acetone*, the true homologue of diethylated acetone, and the isomer of ethylated acetone.

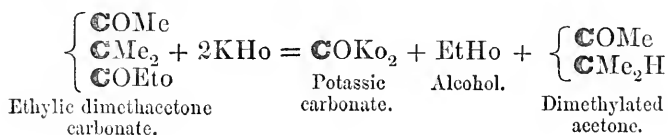
The percentage numbers calculated from its formula,



agree with those obtained in the above analyses.

	Calculated.		Found.		
			I.	II.	Mean.
C ₅	60	69.77	69.41	69.10	69.26
H ₁₀	10	11.63	11.84	11.68	11.76
O	16	18.60			
	<hr/>	<hr/>			
	86	100.00			

The production of dimethylated acetone from ethylic dimethacetone carbonate by the action of alcoholic potash is explained in the following equation:—



Dimethylated acetone is a colourless, transparent, and very mobile liquid, possessing a pleasant odour, reminding at the same time of parsley and acetone. Its specific gravity is 8099 at 13° C., and it boils at 93° 5 C. A determination of its vapour-density

gave the number 2.92. Theoretical density calculated from $C_5H_{10}O = 2$ vols., 2.97.

Dimethylated acetone closely resembles its ethylic homologue in all its chemical properties; like diethylated acetone, it is oxidized with difficulty, and does not very readily form a crystalline compound with hydric sodic sulphite—differing in the latter respect markedly from its isomer, ethylated acetone, and also from methylated acetone described below.

We have mentioned above that the ethereal liquid from which ethylic dimethacetone carbonate was obtained by ebullition with aqueous potash, contained another body probably homologous with ethylic ethacetone carbonate. The analyses of the ethereal liquid before ebullition with aqueous potash indicate the presence of this body, which may be appropriately named *ethylic methacetone carbonate*. These analyses made with the products of several distinct operations, gave the following percentage results.

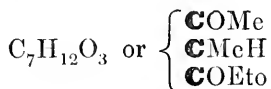
	I.	II.	III.	Mean.
C	59.64	59.66	59.56	59.62
H	8.67	8.73	8.84	8.75

These numbers coincide very closely with those that would be obtained by the analysis of a mixture of equal weights of ethylic dimethacetone carbonate ($C_8H_{14}O_3$) and ethylic methacetone carbonate ($C_7H_{12}O_3$), viz.,

C	59.54
H	8.60

All attempts to separate these two liquids by fractional distillation failed, owing to the close approximation, if not absolute identity, of their boiling-points. In one operation, however, where the action of sodium upon the acetic ether had not been pushed so far, we obtained a product which consisted almost entirely of ethylic methacetone carbonate, as is seen from the following analysis:—

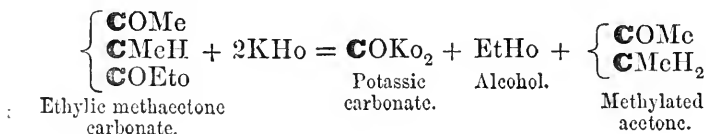
·2624 grm. gave ·5637 grm. carbonic anhydride and ·2017 grm. water, numbers which approach closely to the formula of ethylic methacetone carbonate.



	Calculated.		Found.
C ₇	84	58·33	58·59
H ₁₂	12	8·33	8·54
O ₃	48	33·34	
	<hr/>	<hr/>	
	144	100·00	

Finding that this body had been already obtained in a state of perfect purity by Geuther,* we did not make any further attempts to separate it more completely from ethylic dimethacetone carbonate, especially as its presence in the mixtures above analyzed is proved by the isolation of methylated acetone—its derivative ketone, as described below.

To the properties of ethylic methacetone carbonate described by Geuther, we have only to add that, in opposition to this chemist's statement, it is very readily decomposed by aqueous potash, with the formation of *methylated acetone* according to the following equation:—



Methylated acetone is best obtained in a state of purity by combining it with hydric sodic sulphite, pressing the beautiful crystalline compound so formed between folds of blotting-paper to remove traces of dimethylated acetone, exposing it over sulphuric acid *in vacuo*, and then regenerating the methylated acetone by distillation with aqueous potash. The liquid so obtained, after drying over quicklime and rectification, gave numbers agreeing well with the above formula.

	Calculated.		Found.		
	<hr/>		I.	II.	Mean.
C ₄	48	66·66	66·69	66·40	66·55
H ₈	8	11·11	11·31	11·44	11·37
O	16	22·23			
	<hr/>	<hr/>			
	72	100·00			

Methylated acetone is a colourless, transparent, and very mobile

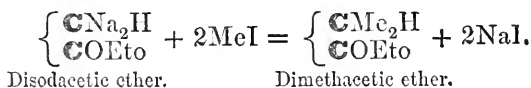
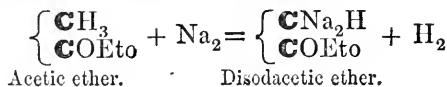
* Gütting. Anzeigen, 1863, p. 281; and Jahresbericht für Chemie, 1863, p. 323.

liquid, possessing an odour like chloroform, but more pungent. It is tolerably soluble in water, and more than slightly so in a saturated solution of common salt. Its specific gravity is $\cdot 8125$ at 13°C . It boils at 81°C ., and its vapour-density is $2\cdot 52$, the theoretical number being $2\cdot 49$.

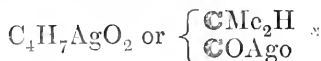
We give below our reasons for concluding that methylated acetone is identical with the ethyl-acetyl described by Freund*, and obtained by acting upon acetylic chloride with zincic ethide.

Methylated acetone forms a splendidly crystalline compound with hydric sodic sulphite, and in its other chemical properties so closely resembles ethylated acetone as to require no further description. It retains alcohol with such tenacity as to render its separation from that liquid, by washing and treatment with calcic chloride, almost impossible. This separation, however, is readily effected by the action of hydric sodic sulphite.

We reserve for a future communication the description of the products derived from the substitution of methyl for hydrogen, in the methyl of acetic ether; but we may mention before leaving the reaction now under consideration, that we have obtained an ether isomeric with butyric ether, the formation of which is explained in the following equations:—



By acting upon this ether with alcoholic potash it is decomposed, yielding alcohol and potassic dimethacetate. On distilling the latter with dilute sulphuric acid, dimethacetic acid, isomeric with butyric acid, is obtained as an oily liquid tolerably soluble in water. Treated with argentic carbonate, it readily gave a crystalline silver-salt, which after being well-washed with water and then dried *in vacuo*, yielded numbers agreeing well with the formula of argentic dimethacetate.



* Ann. Ch. Pharm. cxviii, 1.

		Calculated.		Found.		Mean.
				I.	II.	
C ₄	48	24.61		24.38	24.16	24.27
H ₇	7	3.59		3.65	3.61	3.63
Ag	108	55.38		55.41	55.64	55.52
O ₂	32	16.42				16.58
		<hr/>	<hr/>			<hr/>
		195	100.00			100.00

Action of Sodium and Amylic Iodide upon Acetic Ether.

For this reaction the compounds of sodium derived from acetic ether were prepared as before, and were then submitted to the action of amylic iodide for several hours at the boiling point of the mixture. When the sodium had all become converted into iodide, water was added and the supernatant liquid decanted. We reserve a complete description of this liquid for our next communication, and will here confine ourselves to the separation from it of *œnanthyl*ic acid, which was obtained as follows:—The crude product, after drying over calcic chloride, was submitted to rectification, and the portion boiling between 170° and 190° C. collected apart and decomposed by ebullition with alcoholic potash. By this treatment we destroyed any ethylic amylacetone carbonate and ethylic diamylacetone carbonate that were present, and obtained the potash-salt of an acid derived from acetic acid by the substitution of one atom of amyl for one of hydrogen. The potash-salt thus formed was distilled with excess of sulphuric acid diluted with a large quantity of water. Upon the distillate there floated an oily acid, possessing an odour resembling *œnanthyl*ic acid. This acid was converted into an ammonia-salt, from which a silver-salt was prepared by precipitation. After being well washed with cold water, this salt yielded the following numbers on analysis:—

·2423 grm. gave ·3159 grm. carbonic anhydride, ·1204 grm. water, and ·1108 grm. silver.

These numbers agree well with the formula of argentic amyl-acetate or *œnanthyl*ate.



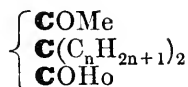
	Calculated.		Found.
C ₇	84	35.44	35.56
H ₁₃	13	5.49	5.52
Ag	108	45.57	45.72
O ₂	32	13.50	13.20
	<hr/>	<hr/>	<hr/>
	237	100.00	100.00

We have also examined the barium-salt, which is an amorphous soapy substance. Dried at 100° C., .2715 grm. gave .1599 grm. baric sulphate, corresponding to 34.62 per cent. of barium. Baric œnanthylate contains 34.69 per cent. of barium. We state our reasons below for believing amylic acid to be identical with œnanthylic acid.

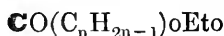
In the foregoing pages we have confined ourselves, as far as possible, to the bare description of experimental results, avoiding any digression to the theoretical considerations which naturally forced themselves upon our attention. It now becomes necessary, however, to take a retrospect of our results, in order to assign to them their proper place amongst chemical phenomena, and to point out their possible bearing upon future investigation in the same direction. In doing this it will be most convenient to discuss the subject under two heads, viz., the considerations involved in the production of the carboketonic ethers derived from the duplication of the molecule of acetic ether, and secondly, those suggested by the substitution of the alcohol radicals for the hydrogen in the methyl of acetic ether.

I. *Constitution and Chemical Relations of the Ethereal Salts and Ketones derived from the Duplication of the Molecule of Acetic Ether.*

There is always a difficulty in assigning to an entirely new series of organic bodies their true position among other families, and this is more especially the case when, like the bodies now under consideration, they exhibit but few obvious relations to other series. It is, therefore, with some hesitation, in regard to the ultimate place that may be assigned to them, that we have ventured to consider these bodies as the ethereal salts of peculiar acids, the latter compounded of the residues of ketones and of carbonic acid, the general formula of these acids being



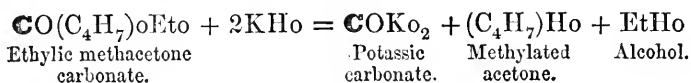
Looking only, however, to the results of the action of caustic alkalies upon the ethylic salts of these acids, and assuming a formula that will most readily explain this action, we arrive at the following very simple expression for these ethereal salts,



This is obviously the formula of carbonic ether,



in which one atom of ethyl is replaced by the radical $\text{C}_n\text{H}_{2n-1}$, belonging to the allyl series; and the action of caustic alkalis upon ethylic methacetone carbonate, for instance, would be expressed as follows:—



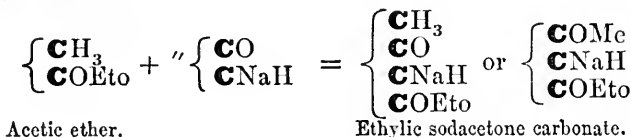
Notwithstanding the very simple expression which is thus given to this reaction, and which is in harmony with Kane's views of the constitution of acetone, we cannot adopt it without complicating other well-marked reactions in the ketone family, and ignoring the very palpable difference between the ketonic and alcoholic families. This alcoholic side of the ketone character, if we may be allowed the expression, supported as it is by the numerous compounds described by Kane, merits more attention than has hitherto been bestowed upon it, and on this account we have drawn attention to its bearings upon the bodies now under discussion, although we have not been able, in its present aspect, to avail ourselves of it in the interpretation of the reactions now under consideration.

In the rational formulæ which we have adopted for the carbo-ketonic ethers, it is not difficult to trace the two original atoms of acetic ether which give rise to the new bodies. To take the production of ethylic methacetone carbonate as an example, it may be assumed that the action of sodium upon one molecule of acetic ether converts the latter into a body equivalent to ethylene

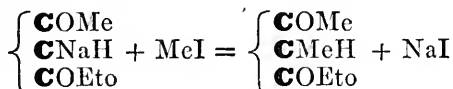




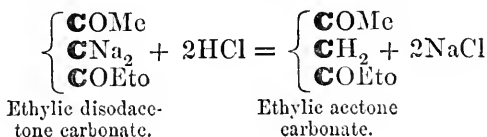
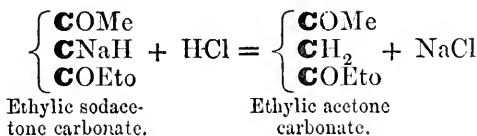
and that this diad body then coalesces with a molecule of unchanged acetic ether, linking together the two radicals of the latter, thus:—



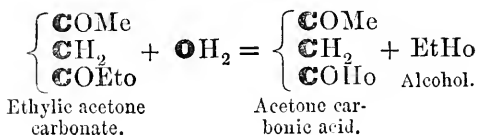
The exchange of sodium for methyl then converts ethylic sodacetone carbonate into ethylic methacetone carbonate.



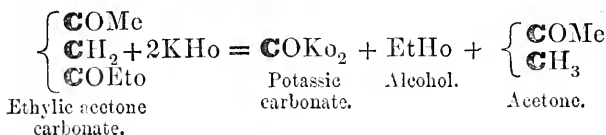
The constitution of the carboketonic ethers here developed indicates the existence of a compound in which the value of n in the above general formula = 0. Such an ethereal salt would be produced by acting with hydrochloric acid upon either ethylic sodacetone carbonate or ethylic disodacetone carbonate.



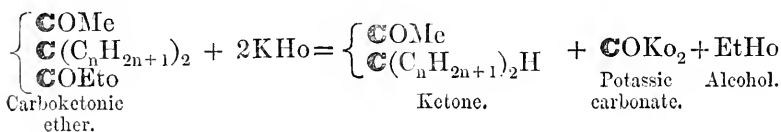
The carboketonic ether thus indicated has actually been obtained by Geuther according to the first of the above equations, and is described by him, in the paper above alluded to, under the name *Di-methylene-carbonic-acid-ethylene ether*. In fact he appears to have also obtained, in a free state, the acid of the above ether, which is formed when the latter is placed in contact with water, although he has not yet submitted it to investigation.



Ethylic acetone carbonate, boiled with excess of baryta-water or alcoholic potash, ought to yield, in accordance with the homologous reactions, alcohol, a carbonate of the base, and acetone, according to the following equation:—



The decomposition of the carboketonic ethers by caustic alkalies is readily traced by the use of the general formulæ above given; besides alcohol, a carbonate of the alkaline metal is produced, whilst a ketone containing three atoms less of carbon than the carboketonic ether is formed.



The composition and mode of formation of the ketones described above, together with the general methods of forming these bodies previously known, indicate the existence of many isomeric compounds belonging to this family alone, without taking into consideration the metameric bodies in the aldehyde and allyl-alcohol series. The formula of acetone,



does not allow the conception of any isomer. The formula of the next higher ketone is equally incapable of isomeric modification, for the formulæ



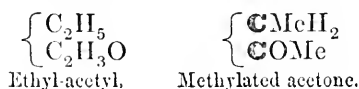
are only apparently isomeric. If reduced to the tetrad carbon type, they both become COMeEt . This is the formula of *methylated acetone*, described above, of *methylacetone* obtained by

Fittig* in distilling lead acetate, and of *ethyl-acetyl* obtained by Freund† in acting upon acetylic chloride with zinc-ethide. Unless physical causes of isomerism be assumed, there can be little doubt as to the identity of these three substances, the only difference known being in their boiling-points, which are as follow:—

	Barometer.
Methylated acetone.....	81° C. about 760 millims.
Ethyl-acetyl.....	77°·5–78° C. about 738 millims.
Methylacetone.....	75°–77° C.

The discrepancy between the first two ceases to be remarkable when the difference of pressure at which their boiling-points were determined is taken into account, and when it is remembered that our methylated acetone probably retained traces of dimethylated acetone which boils at 93°·5 C. Fittig does not give the boiling-point of his methyl acetone as an exact determination, remarking that “a more accurate determination of the boiling-point was obliged to be abandoned on account of the small amount of liquid available.”

The origin of Fittig’s methylacetone does not afford any satisfactory clue to its constitution, but the production of ethyl-acetyl and methylated acetone by synthetical processes, not only confirms the commonly-received view of the constitution of the ketones, but also proves the identity of these two bodies. The formation of ethyl-acetyl by Freund’s process shows that it consists of two bodies of the composition of the radicals indicated by the name, whilst the formula for methylated acetone, above given, if rightly interpreted, affirms the same thing.

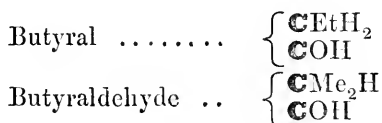


The presence of methyl in the so-called acetyl has been abundantly proved, consequently the chlorous radical is the same in both the above formulæ, whilst the formation of butyric acid, by the substitution of ethyl for hydrogen in the methyl of acetic acid, proves that ethylated methyl is identical with propyl, and that consequently methylated methyl is the same thing as ethyl, therefore the basylous radicals in the above formulæ are also identical.

* Ann. Ch. Pharm. cx, 17.

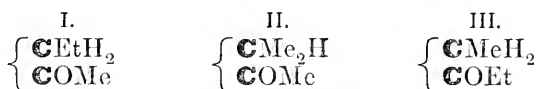
† Ibid. cxviii, 1.

Butyral, which is isomeric with methylated acetone, has been classed by Kekulé amongst the ketones, but we cannot agree with this classification, as, unlike a ketone, it yields on oxidation a fatty acid containing the same number of atoms of carbon, and it also reduces with facility ammoniacal solution of argentic oxide; in fact Kekulé's own definition of a ketone excludes it completely from this class of bodies. Butyral does not appear to be identical with the butyraldehyde obtained by the oxidation of protein bodies, for the first does not, according to Chance, form a definite compound with ammonia, whilst the second does. The two following formulæ possibly express the nature of this isomerism:—



If this hypothesis be correct, the first ought to yield on oxidation normal butyric acid, and the second dimethacetic acid.

When we ascend the ketonic series one step higher, isomerism becomes possible, and the ketonic formula $\text{C}_5\text{H}_{10}\text{O}$ is susceptible of the three following isomeric modifications:—



At first sight it would appear that two other isomers would be produced by the introduction of propyl (CEtH_2) and isopropyl (CMe_2H), thus $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{COPr} \end{array} \right.$ and $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{COPr}\beta \end{array} \right.$; but a closer inspection of these formulæ shows the first to be identical with No. I. and the second with No. II. Thus, reduced to the carbonic-acid type, these formulæ become respectively



All three isomers are now known. The first of the above formulæ is that of ethylated acetone described above, which readily forms a crystalline compound with hydric sodic sulphite. The second is that of dimethylated acetone, which we believe to be identical with the body obtained by Fittig* in distilling lead

* Ann. Ch. Pharm. ex, 17.

acetate, and to which he gave the name ethyl acetone. Both bodies form crystalline compounds with hydric sodic sulphite. The boiling-point of dimethylated acetone is $93^{\circ}5$ C. Fittig states that ethyl acetone boils between 90° and 95° . The only discrepancy between the two compounds is in their specific gravities, which are as follow:—

Dimethylated acetone	·8099 at 13° C.
Ethyl acetone	·812 at 19° C.

This discrepancy may perhaps be explained by the fact that Fittig's ketone yielded on analysis 0·6 per cent. too much carbon, and 0·4 per cent. too little hydrogen, which would indicate that it still contained dumasine, from which it had been approximately separated by fractional distillation.

The name which Fittig has applied to his ketone of the above composition, implies that he regarded it as ethylated acetone, but the boiling-point of the latter (101° C.) precludes this supposition (see remarks about these boiling-points below).

The third of the above formulæ is that of Freund's* ethyl-propionyl prepared by the action of zinc-ethide upon propionyl chloride. This body boils at 101° C. like ethylated acetone, but, unlike the latter, does not form a crystalline compound with hydric sodic sulphite. The origin of Morley's propione,† obtained by the distillation of baric propionate, renders its identity with ethyl-propionyl almost certain. Its boiling-point, 100° C., is nearly the same, and, like ethyl-propionyl, it also, as Freund has proved, refuses to form a crystalline compound with hydric sodic sulphite.

There are still two other compounds of this formula which have been sometimes classed as ketones, but respecting which evidence is still wanting as to whether they belong to the ketone or aldehyde family. These are Limpricht and Uslar's propione,‡ which boils at 110° C., and methyl-butyral,§ which boils at 111° C. The first forms a crystalline compound with hydric sodic sulphite, but it is not known whether or not it reduces ammoniacal solution of argentic oxide. The behaviour of the second with either of these reagents is unknown.

The seven-carbon ketones to which diethylated acetone belongs,

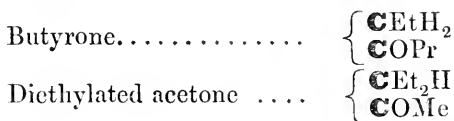
* Ann. Ch. Pharm. cxviii, 1.

† Ibid. lxxviii. 187.

‡ Ibid. xciv. 327.

§ Ibid. lii. 295.

are capable of more numerous modifications, of which however only two are known, viz. :—



The isomerism of these bodies is evident from their origin, and from the difference of 6° in their boiling-points, butyrone boiling at 144° C., whilst diethylated acetone boils at 137 – 139° C. The rise in boiling-point by the successive substitution of the alcohol radicals for the hydrogen of methyl affords a valuable clue to the constitution of numerous organic compounds, and attention has recently been called to this subject by Kolbe,* who has shown that the successive substitution of alcohol radicals for the three atoms of hydrogen in ammonia and in the methyl of methylic alcohol is attended with very different results as regards elevation of boiling-point; thus the addition of CH_2 to aniline $\text{N}(\text{C}_6\text{H}_5)\text{H}_2$ with the production of toluidine $\text{N}(\text{C}_7\text{H}_7)\text{H}_2$ raises the boiling-point about 19° C.; but if the addition of CH_2 to aniline convert the latter into methyl-aniline $\text{N}(\text{C}_6\text{H}_5)\text{MeH}$, then the boiling-point rises only 10° , whilst the replacement of the third atom of hydrogen appears to be attended with a rise of only about 5° C. This observation, so far as the existence of the difference described is concerned, receives considerable support from the boiling-points of the ketones mentioned above, although the actual numerical expression of this difference does not coincide with that given by Kolbe. Thus acetone boils at about 55° C., and methylated acetone at 81° C., the difference being 26° C.; and a comparison of the two formulæ,



shows that acetone is converted into methylated acetone by the substitution of methyl for the *first* atom of hydrogen in methyl. Dimethylated acetone,



boils at $93^\circ\cdot 5$, which is only $12^\circ\cdot 5$ higher than methylated acetone.

* Ann. Ch. Pharm. exxxii, 112.

An inspection of the formula of this body shows that it is derived from methylated acetone by the substitution of methyl for the *second* atom of hydrogen in the methyl of acetone. Again, ethylated acetone is derived from acetone by the substitution of ethyl for the first atom of hydrogen in the methyl of acetone, and its boiling-point is 101° or $23^{\circ} \times 2 = 46^{\circ}$ higher than that of acetone, whilst the boiling-point of diethylated acetone is 138° or $18^{\circ} \cdot 5 \times 2 = 37^{\circ}$ above that of ethylated acetone. In all cases of isomerism it may be safely asserted that the body, containing the fewest atoms of an alcohol radical, substituted for hydrogen, will boil at the highest temperature.

This is clearly seen in the following examples:—

	Name.	Formula.	Boiling-point.
Isomeric ..	Butyral	$\begin{cases} \text{C}^{\bullet}\text{EtH}_2 \\ \text{COH} \end{cases}$.. 95° C.
	Methylated acetone	$\begin{cases} \text{C}^{\bullet}\text{MeH}_2 \\ \text{COMe} \end{cases}$.. 81° C.
Isomeric ..	Methyl-butyral	$\begin{cases} \text{C}^{\bullet}\text{PrH}_2 \\ \text{COH} \end{cases}$.. 111° C.
	Ethylated acetone	$\begin{cases} \text{C}^{\bullet}\text{EtH}_2 \\ \text{COMe} \end{cases}$.. 101° C.
	Ethyl-propionyl	$\begin{cases} \text{C}^{\bullet}\text{MeH}_2 \\ \text{COEt} \end{cases}$.. 101° C.
	Dimethylated acetone ..	$\begin{cases} \text{C}^{\bullet}\text{Me}_2\text{H} \\ \text{COMe} \end{cases}$.. $93^{\circ} \cdot 5$ C.
Isomeric ..	Butyrene	$\begin{cases} \text{C}^{\bullet}\text{EtH}_2 \\ \text{COPr} \end{cases}$.. 144° C.
	Diethylated acetone	$\begin{cases} \text{C}^{\bullet}\text{Et}_2\text{H} \\ \text{COMe} \end{cases}$.. 138° C.

The carboketonic ethers show in a very remarkable manner the boiling-point values of different atoms of hydrogen, whilst the two isomeric bodies of this series also exemplify what has just been stated regarding the inference of constitution from the boiling-point. Reduced to the diadelphic type, these bodies may be thus tabulated:—

Name.	Formula.	Boiling-point.
Ethyl acetone carbonate	$\left\{ \begin{array}{l} \text{C}(\text{CMeO})\text{H}_2 \\ \text{COEtO} \end{array} \right\}$.. 176° C.
Ethyl methacetone carbonate. .	$\left\{ \begin{array}{l} \text{C}(\text{CMeO})\text{MeH} \\ \text{COEtO} \end{array} \right\}$.. 184° C.
Ethyl dimethacetone carbonate	$\left\{ \begin{array}{l} \text{C}(\text{CMeO})\text{Me}_2 \\ \text{COEtO} \end{array} \right\}$.. 184° C.
Ethyl ethacetone carbonate ..	$\left\{ \begin{array}{l} \text{C}(\text{CMeO})\text{EtH} \\ \text{COEtO} \end{array} \right\}$.. 195° C.
Ethyl diethacetone carbonate. .	$\left\{ \begin{array}{l} \text{C}(\text{CMeO})\text{Et}_2 \\ \text{COEtO} \end{array} \right\}$.. 211° C.

It will be seen from these formulæ that the lowest of the carboketonic ethers has already one atom of methylic hydrogen substituted by the radical acetyl (CMeO), consequently the further substitution of methyl and ethyl takes effect upon the second and third atoms of methylic hydrogen. When in the formation of ethyl methacetone carbonate methyl is substituted for the second atom of hydrogen, the boiling-point rises only 8° C.; but when the third atom of hydrogen is in like manner exchanged for methyl the boiling-point is not appreciably affected, ethyl methacetone carbonate and ethyl dimethacetone carbonate both boiling at the same temperature.

The introduction of ethyl in the place of the second atom of hydrogen, in passing from ethyl acetone carbonate to ethyl ethacetone carbonate, raises the boiling-point 19° C., or 9·5 for each addition of CH_2 . Ethacetone carbonate contains CH_2 more than methacetone carbonate, and the addition is also here made to the group occupying the place of the second atom of hydrogen; in this case the addition of CH_2 is also attended by a rise of only 11° in the point of ebullition. Finally, the conversion of ethyl ethacetone carbonate into ethyl diethacetone carbonate, unlike the corresponding change in the methyl compounds, is attended with a marked, though small, rise of boiling-point equivalent to 8° C. for each CH_2 added.

Thus it is evident that the substitution of the same alcohol radical for each of the three atoms of methylic hydrogen is attended with a different result as regards the elevation of boiling-point, and that the rise in the temperature of ebullition becomes markedly less as each atom of typical hydrogen is successively exchanged,

although the absolute thermal values of each of the three atoms depend upon functions which have not yet been discovered.

II. *Constitution of the Fatty Acids.*

There is perhaps no series of organic compounds which has been the subject of such numerous investigations and theoretical speculations as that of the fatty acids; nevertheless the synthesis of several of these acids, by a method of general application described in the foregoing pages, whilst confirming some previous views regarding the constitution of these bodies, has opened a path into their basylous constituent which had not previously been explored, and has disclosed the existence of vast numbers of isomers, which now require only the expenditure of time and labour for their production.

Amongst the investigations and theoretical views above alluded to, we would especially call attention to those of Kolbe and Frankland*, and of Dumas†, which proved the existence of methyl in acetic acid, and of other alcohol radicals in the higher homologues of that acid; to Frankland's view of the constitution of the alcohol radicals themselves, a short abstract of which appeared in the British Association Reports for 1855, Trans. of Sect. p. 62‡; and of Kolbe and Frankland§, who in the year 1857 proposed the derivation of these and a large number of other organic compounds from the carbonic acid or tetratomic

* Memoirs and Proceedings of the Chemical Society, iii, 386, and Ann. Ch. Pharm. lxxv, 288; lxxix, 258.

† Comptes rendus, xxv, 383.

‡ As this abstract does not appear to be generally known, we here copy it from the report in question:—

“These remarkable reactions lead the author to anticipate that zincethyl will prove in the hands of chemists a new and valuable means of research; for it is evident from its reactions that it will be capable of replacing electro-negative elements in organic or inorganic compounds by ethyl; a kind of replacement which has never yet been attempted, but which the author anticipates will enable him to build up organic compounds from inorganic ones, and ascend the homologous series of organic bodies; by replacing, for instance, the hydrogen in a methylic compound by chlorine or iodine, and then acting upon this product of substitution by zincethyl or zinemethyl, the author believes that compounds higher in the series will be obtained, since he regards the higher homologues of methyl and its compounds as derived from the latter radical by the successive replacement of hydrogen by methyl.”

§ Ann. Ch. Pharm. ci, 260.

carbon type ; and, finally, to a recent paper by Kolbe,* in which he predicts the discovery of dimethacetic acid, and of other similarly constituted acids.

We conceive each fatty acid to be formed by the union of a chlorous and a basylous radical. In all acids higher than the formic, these radicals are held together by one of the bonds of a carbon atom in each, as expressed in the following formula of acetic acid :—



Inasmuch, however, as formic acid contains only one carbon radical, the simple basylous radical hydrogen is retained in combination with the compound chlorous radical by the fourth bond of the carbon atom in the latter :



This difference in the constitution of formic acid, as compared with that of the higher members of the same family, makes itself felt in numerous well known abnormal reactions.

The chlorous radical of the fatty acids remains unchanged throughout the entire series, and it is to alterations made in the basylous radical that the separate terms of the series owe their formation.

An inspection of the above formula of acetic acid shows that its basylous radical methyl contains three single atoms of hydrogen combined with a tetrad atom of carbon ; and we have proved, by the production of the synthesized acids above described, that two of these atoms of hydrogen are capable of being exchanged for alcohol radicals, the synthesized acids standing, with regard to acetic acid, in the relations represented by the following formulae :—



Acetic acid.



Ethacetic or butyric acid.



Dimethacetic acid.



Diethacetic acid.

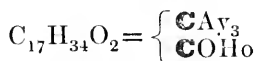


Amylacetic or ænanthylic acid.

Although we have not as yet obtained with certainty acids originating from the substitution of alcohol radicals for more than two

* Zeitschrift f. Ch. u. Pharm. 1864, s. 30.

of the atoms of hydrogen in the methyl of acetic acid,* yet there can be little doubt that the third atom admits of a similar exchange; and we have, in fact, obtained indications of the formation of acids depending upon this threefold replacement—an operation which, carried out with amyl, would obviously produce triamyl-acetic acid, possessing the percentage composition of margaric acid:



It is unnecessary at present to follow the development of this reaction further; but it is evident, from what has been already done, that by a proper selection of the three radicals put into the place of the methylic hydrogen, any fatty acid, from the margaric downwards, can be produced without difficulty.

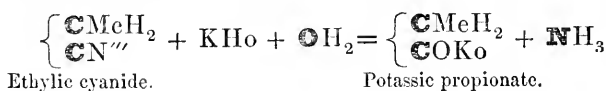
In order to understand the relations between the synthesized and the natural fatty acids, it is necessary to remember the constitution of the latter as revealed in their production from the cyanides of the alcohol radicals; these radicals, of which the cyanides have been so employed, must consist of methyl in which not more than one atom of hydrogen has been replaced, since the alcohols containing them yield by suitable oxidation the corresponding fatty acids; whereas it has been shown by Friedel† that secondary alcohols, such as isopropyl alcohol, in which *two* atoms of methylic hydrogen have been replaced, yield, under the same conditions, ketones instead of acids. Hence the molecules of the normal alcohol radicals must possess the following constitution:—

Methyl.	$\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \right.$
Ethyl or methylated methyl	$\left\{ \begin{array}{l} \text{CMeH}_2 \\ \text{CMeH}_2 \end{array} \right.$
Propyl or ethylated methyl	$\left\{ \begin{array}{l} \text{CEtH}_2 \\ \text{CEtH}_2 \end{array} \right.$
Butyl or propylated methyl	$\left\{ \begin{array}{l} \text{CPrH}_2 \\ \text{CPrH}_2 \end{array} \right.$
Amyl or butylated methyl.	$\left\{ \begin{array}{l} \text{CBuH}_2 \\ \text{CBuH}_2 \end{array} \right.$
&c.	&c.

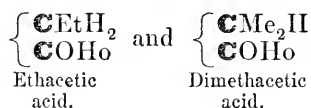
* The authors have since succeeded in effecting this substitution for all three atoms of hydrogen.

† Bulletin de la Soc. Chimique, 1863, p. 247.

and hence when the cyanides of these radicals are boiled with caustic alkalis, they yield acids containing as their basylous constituent, the normal alcohol radicals which were present in the cyanides; thus ethylic cyanide yields potassic propionate—

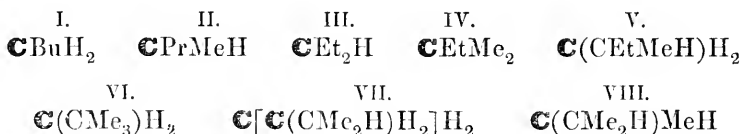


An inspection of the above formula for potassic propionate shows that propionic acid is incapable of isomerism from any change of radicals; and inasmuch as ethyl is simply methylated methyl, it follows that methacetic acid, when obtained by the substitution of one atom of hydrogen in acetic acid by one of methyl, must be identical with propionic acid, which, with acetic acid, can have no isomer depending on a difference of radicals. When, however, we ascend the next step of the series, we find that butyric acid is capable of two, and only two, isomeric modifications, viz. :—



Both these acids have now been synthetically produced, and the first must be identical with butyric acid, since it contains ethylated methyl as its basylous radical—a conclusion which is in perfect harmony with experimented facts, for we have shown above that butyric acid and ethacetic acid are undistinguishable from each other, whilst dimethacetic acid differs in odour and in the crystalline form of its silver-salt.

Ascending now to caproic acid, the number of possible isomers is augmented to eight, this being in fact the number of possible metameric modifications of the basylous radical of caproic acid—amyl, viz. :—



No. I. is normal amyl or butylated methyl; Nos. II., III., and IV. are obvious isomers, whilst the remainder owe their differences to the metameric modification of the radicals butyl and propyl contained in Nos. I. and II.

Of the isomeric acids, those containing the radicals Nos. I. and III. are the only ones known. The first is the caproic acid obtained by the action of potash upon amylic cyanide, and which is probably identical with the caproic acid obtained from cocoa-nut oil; whilst the second is diethacetic acid obtained as above described, and which differs from caproic acid in its odour, in the boiling-point of its ether (which is 11° C. lower than that of caproic ether), in the specific gravity of its ether, and in the crystalline form and solubility of its silver-salt.

Enanthylic acid admits of still more numerous isomeric modifications, of which only one is at present known with certainty, since, for the reasons above given, we believe amylacetic acid to be identical with the acid that would be obtained by the action of potash upon heptylic cyanide, and probably also with that obtained from castor oil and other similar sources.

Now, inasmuch as the acids obtained from the cyanides appear to be identical with the natural or non-synthesized acids of the same atomic weights, and as the alcohol-radicals in these cyanides are normal radicals, that is, methyls in which only one atom of hydrogen has been substituted, it is highly probable that all the non-synthesized acids contain normal radicals with *two* atoms of unexchanged hydrogen, just as the natural acids of the acrylic series contain, as we have proved for a large majority of them,* the largest possible number of atoms of unexchanged hydrogen, which is one atom, thus differing from the synthesized acids of the same series which contain no unexchanged hydrogen, as seen, for instance, in pyroterebic acid and its synthesized isomer ethyl-crotonic acid.



Pyroterebic acid.



Ethyl-crotonic acid.

This remarkable peculiarity in the constitution of the radicals of natural or analytically obtained organic compounds, must be the expression of some general law regulating the formation of those compounds, and which cannot much longer elude detection.

Intimately connected with isomerism in the fatty acids is the like phenomenon in the alcohols which has recently been remarked by Kolbe† and by Friedel‡; in fact the synthesis of the carbo-

* Chem. Soc. J. xviii, 147.

† Zeitschrift f. Ch. u. Pharm. v, 687.

‡ Bulletin de la Soc. Chimique, 1863, p. 247.

ketonic ethers and of the fatty acids lays open a direct path, through the beautiful reactions either of Mendius or Friedel, to corresponding alcohols.

In conclusion, there can be no doubt that the reaction which forms the subject of this paper is capable of a very wide extension, and that by its means we shall be able to ascend many of the well-recognised homologous series. In future communications we hope to give the results of its extension to the alcohols and ethers, and to the benzoic series of ethereal salts.

XLI.—*Action of Acids upon Metals and Alloys.*

By DR. CRACE CALVERT, F.R.S., and RICHARD JOHNSON, F.C.S.

It has frequently occurred to us, in the course of our investigations into the physical properties of metals and alloys, that it would be interesting both in a scientific and practical point of view, if we were carefully to examine the action of some of the acids upon them. We, therefore, submitted copper, zinc, and tin, and the two classes of alloys which are obtained from these metals, viz., brasses and bronzes, to the action of sulphuric, nitric, and hydrochloric acids.

In this series of researches we have followed the same plan as when we experimented upon the "conductibility," the "specific gravity," &c., &c. of metals and alloys; viz., we first examined the action of these acids upon the pure metals, and afterwards upon the alloys composed of the pure metals melted together in equivalent and multiple proportions.

Our experiments having been very numerous, and therefore, having extended over a long period of time, we have deemed it advisable to divide our paper into two parts.

First—The action of sulphuric acid upon zinc, copper, and tin, and of nitric and hydrochloric acids on the same metals.

Secondly—The action of the same acids upon their alloys, viz., brasses and bronzes.

On the marked influence which an Oxidized Surface has on the subsequent action of Sulphuric Acid of various strengths on Zinc.

Before entering into the details of our experiments, it is necessary that we should state, that it was only after considerable time and experience that we were able to determine the exact conditions under which we were to operate, if we wished to obtain constant and correlated results, owing not only to the extreme difficulty attending the preparation of perfectly pure sulphuric acid and a few ounces of pure zinc, but especially to the irregularity of the action of sulphuric acid on zinc, depending, as we observed, upon the peculiar state of its surface. Thus we found that cubes which had been made of the same zinc, but at different times, were acted upon more or less by the same acid when placed under the same circumstances; and these observations gradually led us to the discovery of a curious fact, viz., that a perfectly clean surface of zinc will become, after a few days, sufficiently oxidized by contact with air to modify in a very marked degree the action of sulphuric acid upon it. Thus, if a cube of zinc recently filed is placed in sulphuric acid diluted with 9 eq. water, the action may be considered as null; whilst if the same cube be gently heated in contact with the air and allowed to cool, and be then placed in the same strength of acid, the attack is 10 times greater, as proved by these results.

TABLE.

Quantity of acid	50 cent. cube.
Surface of zinc acted on	1 „
Time of action	2 hours.

STRENGTH OF ACID USED.

Quantity of zinc
dissolved.

SO ₃ .9HO31	{ Used a clean file carefully kept free from grease to clean surfaces of cube.
SO ₃ .9HO03	
SO ₃ .9HO	3 .08	{ After filing washed with alcohol to remove grease. After filing heated in gas flame—allowed to cool before using—surface oxidized.

On the Action of Sulphuric Acid of various Strengths on Zinc.

In looking over the table following these remarks, and containing our results on the action of various strengths of sulphuric

acid on pure zinc with an unoxidised surface, it will be observed, firstly, that they are contrary to the general view entertained by chemists of the action of sulphuric acid upon that metal, for this acid has no action at ordinary temperatures on zinc; also that it requires a temperature of 130° C. before concentrated acid begins to show any marked action, and that it is only at 150° C. that the action of sulphuric acid with 1 and 2 equivalents of water, is fully developed. Secondly, on perusing our results, the following curious facts will be observed, viz., that mono- and bi-hydrated sulphuric acids exercise a comparatively limited action on zinc at a temperature of 130° C. as compared with that of the tri-hydrated acid; thus, whilst SO_3, HO and $\text{SO}_3, 2\text{HO}$ will dissolve only respectively 125 or 236.6 grammes zinc on a square metre surface, $\text{SO}_3, 3\text{HO}$ will in the same space of time dissolve 9860 grammes or 7 to 8 times the amount. Further, the same extraordinary difference of action of these various strengths of acids is maintained when their temperature is raised to 150° C.

A similar difference of action is observed when the action of diluted sulphuric acids on the unoxidized surface of pure zinc is studied; thus when $\text{SO}_3, 6\text{HO}$ acts upon such a metal, only 561.6 grammes per metre surface are dissolved in two hours, whilst $\text{SO}_3, 7\text{HO}$ dissolves in the same space of time as much as 5260.8 grammes, but in this case the temperature employed was only 100° C., or that of the boiling point of the latter acid.

The reactions of sulphuric acid of different strengths upon an unoxidized surface of pure zinc, are far more complicated and interesting than chemists admit. To understand them it is necessary that they should be classed under two distinct heads, viz., the action of SO_3, HO , in which case the metal is oxidized solely at the expense of the acid, sulphurous acid being produced, whilst with $\text{SO}_3, 2\text{HO}$, and especially with $\text{SO}_3, 3\text{HO}$, not only is sulphurous acid given off, but also simultaneously with it sulphuretted hydrogen.

It is interesting to observe two distinct chemical reactions taking place simultaneously; thus we have an action similar to that which sulphuric acid exercises on the metals of the alkalies or alkaline earths, giving rise to hydrogen and a sulphate of the metal, and that which sulphuric acid has, viz., on the fifth group, etc., viz., mercury, generating sulphurous acid and a sulphate of the metal.

Lastly, it will be observed on looking over the table that sul-

phurous acid gradually disappears, whilst the quantity of sulphuretted hydrogen increases, until in its turn it also disappears and is replaced by pure hydrogen.

TABLE 1.

Action of Sulphuric Acid of different strengths upon pure Zinc.

Quantity of acid 50 cent. cubes.
 Surface acted on 1 „ „
 Time of action 2 hours.

Strength of acid.	Temperature degs. cels.	1 centimetre cube.	1 sq. metre.	Remarks.
SO ₃ HO ..	Ordinary	“	“	
“ „ ..	130°	·075	125 0	SO ₂ evolved.
“ „ ..	150°	·232	386 6	SO ₂ evolved. No HS.
SO ₃ 2HO ..	Ordinary	·002	3 3	
“ „ ..	130°	·142	236 6	SO ₂ evolved. A little HS.
“ „ ..	150°	·345	575 0	HS given off and SO ₂ .
SO ₃ 3HO ..	Ordinary	·002	3 3	
“ „ ..	130°	5 916	9860 0	Large quantity of HS. A trace of SO ₂ . Violent action. Large quantity of ZnOSO ₃ undissolved. Same action as above.
“ „ ..	130°	4 916	8193 3	
“ „ ..	150°	5 450	9083 3	
SO ₃ 4HO ..	Ordinary	·005	8 3	
“ „ ..	130°	3 080	5133 3	Large quantity of HS given off, with a little SO ₂ . Violent action. Quantity of ZnOSO ₃ not dissolved.
“ „ ..	130°	2 389	4731 6	
SO ₃ 5HO ..	Ordinary	·049	81 66	
“ „ ..	130°	·456	760 0	Acid nearly boiling. HS given off. Trace of SO ₂ .
SO ₃ 6HO ..	Ordinary	·027	45 0	
“ „ ..	130°	·337	561 6	Boiling point of this acid. HS evolved.
SO ₃ 7HO ..	Ordinary	·018	33 0	
“ „ ..	100°	3 161	5268 3	Violent action at first; after about 20 minutes stopped. ZnO, SO ₃ undissolved. Surface apparently coated, with no HS. Trace of SO ₂ . Attack irregular.
“ „ ..	“	3 800	6333 3	
“ „ ..	“	3 060	5100 0	
SO ₃ 8HO ..	Ordinary	·035	58 3	
SO ₃ 9HO ..	Ordinary	·005	8 3	
SO ₃ 10HO ..	Ordinary	·033	55 3	

Action of Sulphuric Acid on Copper.

The following is the action of 50 cubic centimetres of sulphuric acid, of different strengths, upon 1 cent. cube of pure copper, during a period of two hours, and at the temperature of 130° and 150° C.

TABLE 2.

Action of Sulphuric Acid of different strengths upon pure Copper.

Surface acted upon.....	1 cent. cube.
Quantity of acid.....	50 " "
Time of action	2 hours.
Temperature	130° and 150° C.

Sulphuric acid employed.	Temperature degs. cels.	Loss by 1 cent. cube.	Calculated on 1 sq. metre.	Remarks.
SO ₃ HO	130°	·854	1423·3	Surface of cubes covered with CuS; SO ₂ was also evolved. There was also a residue insoluble in the acid, and composed principally of CuS and CuO·SO ₄ .
" "	"	·704	1173·3	
" "	150°	1·678	2796·7	
SO ₃ 2HO	130°	·008	13·3	Very slight action.
" "	150°	·063	105·0	
SO ₃ 3HO	130°	·004	6·6	
" "	150°	·006	9·9	
SO ₃ 4HO	150°	·000		

These results suggest to us the following remarks: that the temperature at which copper is first attacked by sulphuric acid, SO₃HO, is 130° C., and that even at a few degrees below that temperature, copper is not acted upon; further, that at 150° C., the quantity of copper dissolved by this acid under the same circumstances is nearly the double of that which SO₃2HO, SO₃3HO could dissolve, whilst SO₃4HO, have little or no action upon that metal.

We further noticed, that the decomposition of SO₃HO, by copper is far more complicated than it is generally admitted to be; for the action does not consist simply in the decomposition of the acid into oxygen which oxidizes the copper, and sulphurous acid which escapes, but the affinity of copper for oxygen is such that the whole of this gas is removed from a certain portion of the sulphuric acid, leaving free sulphur, which combines with the copper to form sulphide of copper. The reason which leads us to believe that the formation of this compound is due to the direct combination of the sulphur with the copper, and not, as in the case of zinc, to two chemical actions taking place simultaneously, is that if water were decomposed into its constituent elements, its oxygen uniting with the copper, whilst its hydrogen would com-

bine with the sulphur of the reduced sulphuric acid to form sulphuretted hydrogen, which in its turn would act upon oxide of copper to produce the sulphuret of copper, some sulphuretted hydrogen would undoubtedly have been given off, and under the influence of heat, must have escaped, and have been easily detected. Another proof that sulphuric acid is decomposed into oxygen and sulphur, and that water does not participate in the chemical action which ensues is, that free sulphur volatilizes and condenses in the neck of the small balloons employed, which, in our experiments, were placed in an oil-bath maintained carefully at the required temperature. This remarkable reduction of sulphuric acid by a metal is further corroborated by the action of sulphuric acid upon tin, in which case sulphur is also liberated in considerable quantity, but no sulphide of tin produced, owing, probably, to the fact that sulphur has less affinity for tin than for copper.

TABLE 3.

Action of Sulphuric Acid of different strengths upon Tin.

Sulphuric acid employed.	Temperature degs. cels.	Loss by 1 cent. cube.	Calculated on 1 sq. metre.	Remarks.
SO ₃ HO	150°	3·010	5016·6	A large quantity of SO ₂ given off. No HS. No SSn, but <i>some free sulphur</i> .
SO ₃ 2HO	150°	·640	1066·6	SO ₂ given off. No HS.
SO ₃ 3HO	150°	·470	783·3	SO ₂ given off and a little HS.
SO ₃ 4HO	130°	·215	358·3	A large quantity of HS given off with a little SO ₂ .
SO ₃ 5HO	130°	·140	233·3	Acid nearly on the foil. HS given off, and only a little SO ₂ .

It will be observed, in examining the results contained in this table, that the action of various strengths of sulphuric acid upon tin, differs entirely from that which they exert upon copper, and in some respects on zinc; SO₃HO exerts the maximum action upon copper, but it gradually decreases as the acid becomes more diluted; whilst with zinc, as before stated, the action is completely different

according to the strength of acid; but there is still this similitude between the action of sulphuric acid upon tin and zinc, viz., that with a certain strength of acid, sulphurous acid and sulphuretted hydrogen are given off simultaneously; but this action does not take place with SO_3, HO or $\text{SO}_3, 2\text{HO}$, as the first indication of sulphuretted hydrogen occurs with $\text{SO}_3, 3\text{HO}$, and it is only with $\text{SO}_3, 5\text{HO}$ that large quantities of sulphuretted hydrogen are given off, and only a trace of sulphurous acid. From these results we conclude that when strong sulphuric acid acts upon tin, the metal is oxidized, like on copper, through the action of the acid, whilst with weaker acids water is decomposed, the oxygen fixing itself on the tin or zinc, whilst the hydrogen unites with the sulphur to produce sulphuretted hydrogen; therefore, the action of dilute sulphuric acid upon tin may be considered as two chemical actions occurring simultaneously; moreover sulphate of binoxide of tin is produced and not the corresponding salt of protoxide.

The action of sulphuric acid upon tin throws much light on the formation of sulphide of copper, for in the case of tin, as there is no intense affinity between sulphur and that metal, we observe the production of a large quantity of sulphurous acid, no sulphuretted hydrogen, but a large quantity of free sulphur floating in the liquid, showing a complete deoxidation of the sulphuric acid by both metals; but with this difference, that in the case of tin, sulphur remains free, whilst in that of copper, it combines with it, producing a sulphuret.

Action of Nitric and Hydrochloric Acids on Tin, Zinc, and Copper.
—We shall reserve details of our experiments until we describe the results obtained by acting with the same acids on the two classes of alloys formed by these metals, viz., brasses and bronzes; for it was found by direct experiment that to arrive at any correct data, it was necessary to employ acids of peculiar strength, or otherwise the reactions were so complicated that no comparative results could be obtained of the action of these acids on the various groups of alloys. The following facts will, we believe, illustrate these statements:—

TABLE 4.

Action of Nitric Acid upon an Alloy of Copper and Zinc.

Surface acted upon.....	1 cent. cube.
Quantity of acid	100 „
Time of action	24 hours.
Composition of Brass {	1 eq. copper.... 49·059
	1 eq. zinc..... 50·941
	<hr/> 100·000

Strength of nitric acid employed.	Total quantity dissolved on 1 c.c.	Composed of	Per cent.	Average per cent.
Sp. gr.				
Strong acid.	1·14	6·421	48·232 Cu	48·258 Cu 51·742 Zn
		3·328 Zn	51·768 Zn	
		<hr/> 6·421	<hr/> 100·000	
	3·936	1·898 Cu	48·283 Cu	
		2·038 Zn	51·717 Zn	0·000
		<hr/> 3·936	<hr/> 100·000	
Weak acid.	1·08	1·504	16·856 Cu	16·741 Cu 83·259 Zn
		1·243 Zn	83·144 Zn	
		<hr/> 1·495	<hr/> 100·000	
	2·034	0·340 Cu	16·626 Cu	
		1·705 Zn	83·374 Zn	100·000
		<hr/> 2·045	<hr/> 100·000	

In perusing the above table, it will be seen that whilst nitric acid of sp. gr. 1·14 dissolves the metals composing the brass in the exact proportions in which they exist in the alloy employed, whilst an acid of about half the strength, or of sp. gr. 1·08, dissolves nearly the whole of the zinc contained in the alloy, and only a small quantity of copper. This result, among others, showed us the necessity of employing a given strength of acid in order to conduct a series of comparative experiments on various alloys, and we consider the action of nitric acid of sp. gr. 1·14 a normal action, as it attacks both zinc and copper in the proportions in which they exist in the alloy, whilst that of a stronger or weaker

acid is abnormal, as it acts according to its strength, more or less, on each of the metals composing a brass alloy. These results were further confirmed by a cube of an alloy composed of equal parts of zinc and copper, being left for several days in hydrochloric acid of full strength, the whole of the zinc, or nearly so, of the alloy, being dissolved, leaving a cube which had the same diameter as if it had only been experimented upon, and was composed of nearly pure copper.

The following table illustrates this fact:—

TABLE 5.

Action of Strong Hydrochloric Acid on the Alloy ZnCu.

1 eq. copper	49·059
1 eq. zinc.....	50·941
	<hr/> 100·000

Strength of acid used.	Weight of cube.	Amount of zinc dissolved 1 c.c.	Amount of Zn left in cube.	Remarks.
1·20	grammes. Cu 4·409 Zn 4·577 <hr/> 8·986	4·443	·130	The cubes, after the experiment, have copper-like colour, and have the same diameter as before, but are quite soft. A trace only of copper dissolved.
1·20	Cu 4·467 Zn 4·638 <hr/> 9·105	4·330	·308	

Action of weak Nitric Acid on Brasses.

We shall now proceed to describe the action of weak nitric acid sp. gr. 1·100 on various alloys of zinc and copper, combined in equivalent and multiple proportions. We decided to use this strength of acid, as we found, after many experiments, that this was the best strength of acid that could be employed to obtain constant results.

The table which follows these remarks contains a summary of our results, and gives an idea how varied is the action of the same strength of nitric acid on the same class of alloys, and what an extraordinary influence a few per cent. of copper or zinc, more or less, exerts in preventing or promoting the action of this acid.

Further, in perusing the table, it will be observed that the action of the acid is comparatively violent on all the alloys containing an excess of zinc, and that it is nearly 1,000 times less active on all those in which there is an excess of copper; and we cannot in this case refrain from drawing special attention to the action of the acid on the alloy ZnCu, as compared with that which it exerts upon Zn₂Cu, although there is only a difference of 17 % of zinc.

It is necessary that we should explain how we have arrived at the data found in the fourth column. The figures represent the calculated results of the amount of metals which should have been dissolved had the metals been free, and had not the presence of one of the metals interfered with the chemical action. It will be observed, in comparing these figures with those which represent the quantity of alloy actually dissolved, that in the first four alloys of the table, viz., those which contain an excess of zinc, the quantity of alloy dissolved is in excess of that which theory indicates, whilst in the alloy composed of equivalents of each metal, and those which contain an excess of copper, the action is 40 or 50 times less. These facts appear to us not only interesting in a scientific point of view, but important in their applications to manufactures, especially for brass taps, pipes, &c.

The following is a summary of our experiments:—

TABLE 6.

Action of Nitric Acid, sp. gr. 1·100, on Alloys of Copper and Zinc (Brasses).

Surface acted upon.....	1 cent. cube.
Quantity of acid.....	25 „ „
Time of action.....	15 minutes.
Temperature	20° C.

Metals and composition of alloys.	Loss by 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to the composition of the alloys.
Copper	0·009	15·000	15·000
Zinc	1·760	2933·3	2933·3
Zn ₂ Cu			
Zn 83·70	2·025	3375·0	5457·645
Cu 16·30			
100·00			

TABLE 6—*Continued.*

Metals and composition of alloys.	Loss on 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to the composition of the alloys.
Zn_1Cu			
Zn 80.43	1.740	2900.0	2362.2
Cu 19.57			
<u>100.00</u>			
Zn^2Cu			
Zn 75.36	1.695	2825.0	2214.25
Cu 24.64			
<u>100.00</u>			
Zn_2Cu			
Zn 67.26	1.530	2550.0	1977.8
Cu 32.74			
<u>100.00</u>			
ZnCu			
Zn 50.95	0.027	45.000	1494.0
Cu 49.05			
<u>100.00</u>			
ZnCu_2			
Zn 33.94	0.015	25.000	1005.48
Cu 66.06			
<u>100.00</u>			
ZnCu_3			
Zn 25.52	0.013	21.66	759.75
Cu 74.48			
<u>100.00</u>			
ZnCu_4			
Zn 20.44	0.015	25.00	611.50
Cu 79.56			
<u>100.00</u>			
ZnCu_5			
Zn 17.05	0.010	16.66	512.57
Cu 82.95			
<u>100.00</u>			

Action of Hydrochloric Acid, sp. gr. 1·05 on Alloys of Zinc and Copper (Brasses).

It will be observed, in perusing the results consigned in the table following, that the action of this acid is nearly equal to that which theory indicates on the alloys Zn_5Cu and Zn_4Cu , whilst in the next alloy, Zn_3Cu , which contains only 5 % more copper than the preceding one, the attack is only half of that indicated by theory. But certainly the most unexpected result arrived at, is the complete inaction of hydrochloric acid upon all the alloys containing an excess of copper, and especially on the alloy composed of equivalent proportions of each metal; and it is very remarkable that whilst half the cube of the alloy Zn_5Cu is dissolved in the space of one hour, the alloy with equal equivalents of each of the metals remains perfectly unattacked.

The fourth column in this table also gives the theoretical quantity that should have been dissolved if the metals had been free, and not alloyed.

TABLE 7.

Surface acted upon 1 centimetre cube.
 Quantity of acid..... 50 „ „
 Time of action 1 hour.

Metals and composition of alloys.	Loss on 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to the composition of the alloys.
Copper	0·000	0 000	0 000
Zinc	0 200	333·33	333 33
Zn_3Cu			
Zn 83·70	0·155	258·334	279 00
Cu 16 30			
<u>100·00</u>			
Zn_4Cu			
Zn 80·43	0·155	258 334	268 0
Cu 19 57			
<u>100·00</u>			
Zn_5Cu			
Zn 75·36	0·035	108 334	251·2
Cu 24·64			
<u>100·00</u>			

TABLE 7—*Continued.*

Metals and composition of alloys.	Loss on 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to the composition of the alloys.
Zn_3Cu Zn 67.26 Cu 32.74 <hr/> 100.00	0.050	83.334	224.2
ZnCu Zn 50.68 Cu 49.32 <hr/> 100.00	0.000	0.000	168.933
ZnCu_2 Zn 33.94 Cu 66.06 <hr/> 100.00	0.000	0.000	113.133
ZnCu_3 Zn 25.52 Cu 74.48 <hr/> 100.00	0.000	0.000	85.066
ZnCu_4 Zn 20.44 Cu 79.56 <hr/> 100.00	0.000	0.000	68.133
ZnCu_5 Zn 17.05 Cu 82.95 <hr/> 100.00	0.000	0.000	56.83

Action of Sulphuric Acids SO_3HO and SO_3HIO on Alloys of Copper and Zinc.

We now pass on to the action exerted by the two above mentioned strengths of sulphuric acid upon brasses, the results of which are not less instructive than those already referred to. But before drawing attention to the leading facts observed, it is necessary that we should give the reason why we employed in preference SO_3HO and SO_3HIO for our experiments. They are that SO_3HO is the only acid which attacks copper, in any marked degree; SO_3HIO , the only one which has a corres-

ponding action upon zinc, and therefore by employing these successively upon the same alloy at a temperature of 150°C ., we were acting under favourable circumstances for appreciating the exact mode of action of these acids on both metals entering into the composition of the alloy.

TABLE 8.

Action of Monohydrated Sulphuric Acid on Brasses.

Surface acted upon	1 cent. cube.
Quantity of acid employed	50 „
Time of action	2 hours.
Temperature.....	150°C .
	0 sq. metre.
Action on 1 c. c. of copper	$1.678 = 27.97$
„ „ 1 „ „ zinc	$.232 = 33.67$

Composition of alloys.	Loss on 1 c. c.	Calculated loss 1 sq. metre on surface.	Theoretical loss.	Remarks.
CuZn_3 83.7 Zn 16.3 Cu <hr/> 100.0	.098	163.33	779.5	$\left. \begin{array}{l} \text{SO}_2 \text{ given off. No H}_2\text{S,} \\ \text{and only Zn dissolved.} \end{array} \right\}$
CuZn_4 80.43 Zn 19.57 Cu <hr/> 100.00	.074	123.33	858.3	
CuZn_3 75.36 Zn 24.64 Cu <hr/> 100.00	.180	300.0	980.5	
CuZn_5 67.26 Zn 32.74 Cu <hr/> 100.00	.083	183.3	1175.8	$\left. \begin{array}{l} \text{SO given off.} \\ \text{SO, given off. No H}_2\text{S.} \\ \text{Strong action. Insoluble} \\ \text{residue consists of ZnO,} \\ \text{SO}_2, \text{CuO, SO}_3. \text{ Also a} \\ \text{small quantity of CuS} \\ \text{and S.} \end{array} \right\}$
CuZn 50.68 Zn 49.32 Cu <hr/> 100.00	1.297	2161.6	1375.7	
				The quantities of the metals dissolved were found to be in the exact proportion of those in the alloys.

TABLE 8—*Continued.*

Composition of alloys.	Loss on 1 c. c.	Calculated loss 1 sq. metre on surface.	Theoretical loss.	Remarks.
Cu_3Zn 33.94 Zn 66.06 Cu <hr/> 100.00	1.292	2158.3	2015.0	} SO_2 given off. No HS. A small quantity of free S and CuS .
Cu_3Zn 25.52 Zn 74.48 Cu <hr/> 100.00	1.747	2211.66	2182.01	
Cu_4Zn 20.44 Zn 79.56 Cu <hr/> 100.00	1.328	2213.0	2304.47	Ditto
Cu_5Zn 17.05 Zn 82.95 Cu <hr/> 100.00	.605	1008.33	2386.19	Ditto

In examining the results contained in this table, several interesting data are brought out, viz., that in all the alloys in which there is an excess of zinc over the quantity of copper, the attack is exceedingly limited, whilst in all those in which there is an excess of copper, the action is most marked, and very similar, in fact, to that which acid exerts on pure copper.

It is certainly interesting to observe the extraordinary preventive influence which a metal like zinc has on the action of such a powerful acid as SO_3, HO on copper; and certainly, *a priori*, such a result could have been expected. And we cannot help drawing attention to the striking difference between the action of SO_3, HO on the alloys ZnCu and Zn_2Cu , and, therefore, the influence which only 17 % of zinc exercises in preventing the action of the acid, the action on ZnCu being nearly 15 times as violent as on Zn_2Cu .

It may be further observed that when SO_3, HO acts upon the above alloys, in all those containing an excess of zinc, not only does the zinc prevent the action of the acid upon

the alloy itself, but it so thoroughly preserves the copper from the action of the acid, that whatever may be the amount dissolved, it is represented by zinc only; whilst in the alloys containing an excess of copper, the copper is attacked also, and dissolved in large quantities. As to the general result of the chemical action of $\text{SO}_3, \text{H}_2\text{O}$ on the same group of alloys, we may add that the secondary products are the same as when $\text{SO}_3, \text{H}_2\text{O}$ acts upon copper itself.

Action of $\text{SO}_3, \text{H}_2\text{O}$ on Brasses.

It will be seen, in perusing the results contained in the table which follows these remarks, how very different is the action of $\text{SO}_3, \text{H}_2\text{O}$ as compared with $\text{SO}_3, \text{H}_2\text{O}$ on the same alloys when placed under identical circumstances, for all the alloys which contain an excess of zinc are those most attacked, whilst this strength of sulphuric ($\text{SO}_3, \text{H}_2\text{O}$) acid exerts little or no action upon the alloys containing an excess of copper; and what enhances the value of these results is, that all the alloys which contain an excess of either copper or zinc are attacked more or less, whilst the alloy CuZn is not acted on, and therefore this alloy could be employed with marked advantages for many purposes, the more so that when well prepared it has a fine and rich brass appearance, notwithstanding the large proportion of zinc; it contains about 15 % more than the poorest brass alloys usually found in commerce.

Lastly, it will be observed, that among the secondary products formed during the chemical action of $\text{SO}_3, \text{H}_2\text{O}$, there is no sulphide of zinc produced, as in the case when $\text{SO}_3, \text{H}_2\text{O}$ acts upon the same alloys of zinc and copper.

TABLE 9.

Surface acted upon	1 centimetre cube
Quantity of acid	50 " "
Time of action	2 hours
Temperature	150° C.
	on sq. metre of surface.
Action on 1 c. c. of copper	006 = 10000
" " 1 " zinc	5450 = 9085150

TABLE 9—*Continued.*

Composition. of alloys.	Loss on 1 c. c.	Calculated. on 1 sq. metre.	Theoretical quantity.	Remarks.
CuZn ₃	·135	225 ·0	7605 ·73	SO ₂ given off. No HS. deposits. CuS.
CuZn ₁	·130	216 ·0	7308 ·95	Ditto. A trace of HS.
CuZn ₃	·120	200 ·0	6848 ·86	Ditto
CuZn ₂	·115	191 ·6	6113 ·77	Ditto
CuZn	·090	—	4609 ·2	—
Cu ₂ Zn	·119	198 ·33	3090 ·05	SO ₂ given off.
Cu ₃ Zn	·006	10 ·0	2325 ·95	Ditto
Cu ₄ Zn	·007	11 ·6	1864 ·95	Ditto
Cu ₅ Zn	·006	10 ·0	1557 ·29	Ditto

Action of Acids on Bronzes, or Alloys of Copper and Tin.

We shall follow the same order in examining the action of various acids upon bronzes as we have done in describing their action upon brasses; thus we shall first examine the action of nitric acid, then that of hydrochloric acid, and, finally, that of sulphuric acids; and it is easy to conceive that the action of these various acids upon bronze alloys must be very different, *nitric acid* possessing the property of acting upon both metals, *hydrochloric acid* of acting only upon tin and not upon copper, whilst *sulphuric acid* only acts upon both metals, but under the influence of heat.

We shall now proceed to examine the action of each acid separately.

TABLE 10.

Action of Nitric Acid, sp. gr. 1·25, on Alloys of Copper and Tin (Bronzes).

Surface acted upon 1 cent. cube
Quantity of acid 25 „
Time of action 15 minutes

Metals and com- position of alloys.	Loss on 1 c.c.	Calculated on 1 sq. metre.	Calculated loss according to the composition of the alloys.
Copper.....	1 ·920	3200 ·0	3200 ·0
Tin.....	0 ·595	841 ·667	841 ·667
Sn ₃ Cu			
Sn .. 90 ·27			
Cu .. 9 ·73			
100 ·00	1 ·130	1883 ·33	1071 ·132

TABLE 10—*Continued.*

Metals and composition of alloys.	Loss on 1 c.c.	Calculated on 1 sq. metre.	Calculated loss according to the composition of the alloys.
Sn_3Cu Sn .. 88·14 Cu .. 11·86 <hr/> 100·00	0·725	1208 33	1121·36
Sn_2Cu Sn .. 84·79 Cu .. 15·21 <hr/> 100·00	0·590	983·33	1200·36
Sn_2Cu Sn .. 78·79 Cu .. 21·21 <hr/> 100·00	0·240	400·00	1341·869
SnCu Sn .. 65·02 Cu .. 34·98 <hr/> 100·00	0·110	183·334	1666·6
SnCu_2 Sn .. 51·83 Cu .. 48·17 <hr/> 100·00	0·125	208·334	1977·676
SnCu_3 Sn .. 38·21 Cu .. 61·79 <hr/> 100·00	0·560	933·334	2298·88
SnCu_4 Sn .. 31·73 Cu .. 68·27 <hr/> 100·00	0·910	1516·66	2453·384
SnCu_5 Sn .. 27·10 Cu .. 72·90 <hr/> 100·00	0·485	808·334	2577·725

The first result which attracts attention is that none of the alloys are acted on to the same extent as pure copper; therefore the presence of tin in the alloys counteracts to a certain extent the action of nitric acid on bronzes; but the preventive influence of tin presents this particularity, that the action of the acid increases as the proportion of tin increases; thus the alloy CuSn_5 is attacked ten times more than the alloy CuSn .

It should also be noticed that the quantity of metals dissolved is less in all the alloys containing an excess of copper, as well as in the two alloys Sn_2Cu and Sn_3Cu , than theory indicates, but it is especially with the alloys Sn_2Cu and SnCu that this result is observed.

TABLE 11.

Action of Hydrochloric Acid, sp. gr. 1.10, on Alloys of Copper and Tin (Bronzes).

Surface acted upon	1 cent. cube.
Quantity of acid.....	50 "
Time of action	1 hour.

Metals and composition of alloys.	Loss on 1 c.c.	Calculated on 1 sq. metre.	Calculated loss according to the composition of the alloys.
Copper	0.002	3.334	3.334
Tin	0.011	18.334	18.334
Sn_5Cu	0.017	28.334	16.874
Sn_4Cu	0.016	26.667	16.554
Sn_3Cu	0.015	25.000	16.052
Sn_2Cu	0.012	20.000	15.152
SnCu	0.006	10.000	13.086
SnCu_2	0.006	10.000	11.107
SnCu_3	0.005	8.334	9.065
SnCu_4	0.004	6.667	8.093
SnCu_5	0.003	5.000	7.398

In this series of experiments, the action of hydrochloric acid upon tin is marred by the presence of copper, the action of acid on the bronzes decreasing as the quantity of copper in the alloy increases.

TABLE 12.

Action of Sulphuric Acid (SO³HO) upon Bronze.

Surface acted on 1 cent. cube
 Quantity of acid 50 „
 Time of action 2 hours
 Temperature..... 150° C.

sq. metre.

Action upon 1 c. c. Cu = 1·678 = 2797·2

„ „ Sn = 3·010 = 50·17·6

Composition of alloys.	Loss on 1 cent. cube.	Calculated on 1 square metre.	Calculated loss according to the composition of the alloy.	Remarks.
CuSn ₅ 9·73 Cu 90·27 Sn <hr/> 100·00	·656	1093·3	4801·55	SO ₂ given off. No H ₂ S.
CuSn ₄ 11·86 Cu 88·14 Sn <hr/> 100·00	·546	910·0	4754·26	Ditto Ditto
CuSn ₃ 15·55 Cu 84·45 Sn <hr/> 100·00	·634	1056·6	4672·32	Ditto Ditto
CuSn ₂ 21·21 Cu 78·79 Sn <hr/> 100·00	·525	875·0	4546·65	Ditto Ditto
CuSn 34·98 Cu 65·02 Sn <hr/> 100·00	·632	1053·3	4240·9	Ditto Ditto
Cu ₂ Sn 51·83 Cu 48·17 Sn <hr/> 100·00	·797	1328·3	3866·76	Ditto Ditto

TABLE 12—*Continued.*

Composition of alloys.	Loss on 1 cent. cube.	Calculated loss on 1 square metre.	Calculated loss according to the composition of the alloy.	Remarks.
Cu_3Sn 61.79 Cu 38.21 Sn <hr/> 100.00	.820	1366.6	3645.6	SO ₂ given off. No H ₂ S.
Cu_3Sn 68.27 Cu 31.73 Sn <hr/> 100.00	.450	750.0	3501.33	Ditto Ditto
Cu_5Sn 72.9 Cu 27.1 Sn <hr/> 100.00	.372	620.0	3391.93	Ditto Ditto

In examining the results contained in this table, it will be observed that copper retards the action of the acid upon tin, none of the alloys being attacked in the ratio of the quantity of tin it contains compared with that of copper; in fact, an alloy Sn_3Cu , although it contains 90 % tin and only 10 % copper, is not attacked more than an alloy SnCu , which contains 65 % tin, and 35 % copper. Again two of the alloys which contain a great excess of copper, viz., SnCu_4 and SnCu_5 , are less attacked than any of the other alloys comprised in the series, and it is difficult to understand why the two alloys SnCu_2 and SnCu_3 should be attacked with such violence as compared with the two bronzes which contain a larger amount of copper; the only explanation we shall offer of this exceptional result is, that in our experiments on the "conductibility for heat by metals and alloys," we found that those two alloys had conducting power which differed from all the rest of the alloys of copper and tin, and we submitted at that time the opinion, that it was highly probable that those two alloys were not simply mixtures of metals, but definite compounds, and the exceptional action which SO_3HO has on these alloys, as compared with that it exerts upon the rest of the series, appears to substantiate this view.

XIII.—*On Determining the Weight of Heterogeneous Liquids.*

By HERMANN SPRENGEL.

THE relation between mass, volume, and density furnishes a ready means of determining the weight of a body, and is often resorted to when the result cannot be conveniently arrived at by means of the balance. This, for obvious reasons, applies especially to liquids, and, moreover, to large quantities of liquids. If the liquid is homogeneous, and the space which it fills easily measurable, no difficulty will be experienced in the determination; but if either one of these conditions be unfulfilled, the case is different. It is probable indeed that errors often arise from want of attention to the heterogeneity of liquids.

Take for example the determination of the weight of sulphuric acid accumulating at the bottom of the leaden chambers. In this case we have on the average an area of about 2,000 square feet, covered with acid of a heterogeneous gravity, and varying in height from fractions of an inch to 12 inches or more. We have, then, to ascertain, in the first place, the volume of this liquid, and in the second its average specific gravity.

Determination of the Volume.

As the area of the pan containing the acid, once determined, remains the same in all future determinations, we merely need, on repeating them, to take notice of the altered height of the level. This is commonly effected by plunging a dry gauge perpendicularly into the acid; but by the use of the instrument which I am about to describe we may dispense with the necessity for a separate determination of the height, and ascertain it in a similar, but perhaps superior, way in the course of determining the average specific gravity.

A graduated scale, etched on a plate of glass forming part of the side of the chamber, would doubtless be the most direct and certain way; but practical objections render it inapplicable. Graduated syphons, U tubes, and communicating vessels in general are useless for the determination of the height of heterogeneous liquids, as the heights of the two liquid columns, when in equili-

brium will, of course, be inversely proportional to the specific gravities of the liquids they respectively contain.

Determination of the Average Specific Gravity.

A heterogeneous liquid in equilibrium may be regarded as consisting of an infinite number of laminæ of different gravities, of which the lighter ones are buoyed up by the heavier. Suppose, now, that we have to determine the average specific gravity of such heterogeneous liquid, which we cannot convert into a homogeneous one by mechanical agitation, it is obvious that if a vertical section of this liquid could be procured, the gravity of that section would represent that of the whole, provided that the bottom of the vessel were parallel with the surface of the liquid.

FIG. 1.



With this object I have constructed the instrument represented in the annexed diagrams. A B (fig. 1) is a graduated cylindrical glass tube of about 1 inch diameter and 18 inches in length. It is essential that the calibre of this tube be as nearly as possible the same throughout the whole length. On plunging such a glass tube, open at both ends, vertically into the acid, the liquid will stand at the same height both inside and outside the tube, and at corresponding altitudes will possess the same specific gravity. This cylinder of acid, cut, so to speak, out of the whole mass, has to be withdrawn, its height read off on the scale, and its specific gravity, after mixture, determined in the usual way. The idea which first suggests itself is to affix to the end A a valve (opening towards the inside), which would, on the tube being raised, prevent the liquid from running out. As, however, a certain pressure, equivalent to the resistance of the valve, is required to keep it open, the level inside the tube will always be lower than outside. The chief obstacle to this plan lies in the possible presence of solid particles, which might happen to prevent the valve from shutting, and would render the whole determination useless. To obviate these difficulties I have adopted the follow-

ing expedient. Supposing the liquid column inside the tube were hermetically shut off above its level from the outer air, and in such a manner that no air whatever remained enclosed with the liquid, it is evident that theoretically the column might be raised out of the acid without any loss. As we know that these conditions cannot practically be fulfilled, I have approached them by supplying the tube with a moveable piston attached to another glass tube of small calibre, which serves to adjust the position of the piston to the height of the acid, and for the escape of air, while the acid is entering from below. After this is done, the piston-tube, having at its upper end a piece of black india-rubber tubing, is closed with a common pinch-cock. The instrument might now be lifted out of the acid, and as a tube of this size would lose its charge directly, I have prevented such escape by attaching to its end A a sort of cap, as shown in fig. 2. This cap, which in the diagram is represented detached from the tube, consists of a thin plate, best made of platinum, of a diameter a trifle larger than that of the glass tube. To prevent its slipping off, it is fixed unto the tube by means of two springs, each of which is supplied with a small pin, fitting a corresponding hole bored in the side of the glass tube, without, of course, completely perforating it. There are also, as will be noticed in the figure, four small pieces of platinum fixed opposite to each other round the margin of the cap. These prevent the rim of the glass tube from touching the plate, and thus leave a small space of about $\frac{1}{20}$ th of an inch between the tube and the cap, by which the acid can enter.

FIG 2.



The piston is made of vulcanised india-rubber, cut out of a flat block of that substance with a sharp cork-borer well lubricated with oil. As the accurate fit of the piston is essential, I may mention that a piston a little too small may be enlarged to the required size by boring the central hole somewhat smaller than the piston-tube it is to receive. To secure a sufficient attachment of the piston to the piston-tube, the end C of the latter is

roughened with a file, and the upper part of the piston bound with a strip of india-rubber.*

The piston-tube is, of course, as long as, or even a little longer, than A B, and its diameter about 0.3 inch, while that of the bore ought to be not much less than 0.08 inch; for on immersing A B in the acid, the levels inside and outside the tube ought to be always equal, and as no acid can enter without pressing a proportional bulk of air through the capillary tube, the motion downwards would become inconveniently slow if the bore were much less. To keep C D in the centre of A B, a loose cap of ebonite is affixed at B, serving as a guide.

The scale on A B is etched into the glass, as described in Bunsen's Gasometry. The division is 0.1 inch, subdivided into five parts. Fig. 2 is intended to represent the natural size. The 0-point is placed near the rim, say 0.4 inch above the lower surface of the platinum-plate, when affixed to the tube. This value 0.4 has consequently to be added to all readings, so that 5 inches, read on the scale, is in reality 5.4 inches. As the naked eye can without difficulty distinguish the half between two of these small divisions, we are able to read in this manner 0.01 inch. This accuracy is not superfluous, since in this case one of these small divisions represents a weight of about 300 lbs. of acid.

As the piston, for the sake of accurate reading, must be placed high enough, not to be in contact with the surface of the acid (or more properly the meniscus), and as a certain amount of air remains also enclosed in the capillary tube C D, the amount of both (which we will henceforth call v) necessarily leads to an error when the instrument is withdrawn from the bulk of the acid. For whereas v was previously under the full pressure of the atmosphere, it is now under the pressure of the atmosphere minus the weight of the column of acid in A B. The bulk of v will consequently expand and expel a proportional quantity of acid. All readings will therefore

* This tying of india-rubber tubing, etc., with india-rubber I manage as follows: I cut from a sheet of clean black india-rubber a strip, say a quarter of an inch broad, and of the requisite length. Then, after warming it, I proceed to coil it round the place I wish to tighten, stretching the strip as much as it will bear without tearing, and thus extending it into a long fine membrane. Though each round of such elastic binding exercises only a slight pressure, the sum of all these pressures amounts to something considerable, and the coils compress each other into a solid, compact collar of considerable strength. This binding of india-rubber I recommend as superior to string or wire, as it withstands the action of acids excellently, and does not cut the substance bound with it.

be this much too low. This error is, however, small, as will be seen from the following calculation.

Suppose that the distance of the piston were always kept 0·2 inches above the level of the acid, what would the error amount to at different heights and different gravities of acid if the instrument had the dimensions previously given? The volume of v in this instance was found to be 0·232566 cub. inches, easily deducted from the weight of water, filling 0·2 inches lineal of A B, and the whole of the capillary tube C D.

Supposing the acid in the chamber be 1·5 sp. gr., and its height 1 inch :

v under the atmospheric pressure minus

1 inch acid of 1·5 sp. gr.	= 0·233100 cub. inches
v under the atmospheric pressure	= 0·232566 „
Increase of v	= 0·000834 „

Now we know from the determination of the volume of v that

0·125226 cub. inches occupy 0·2 inch lineal of A B, hence
 0·125226 : 0·2 = 0·000834 : x .

x = 0·00133 inch, representing the number which expresses in lineal inches the increase of v on the scale of our instrument, if it is withdrawn from a depth of 1 inch of acid at 1·5 sp. gr. This number, which represents the error, we will call e .

In like manner are obtained the values of e in the annexed table at the specified heights and gravities :—

	1·5 sp. gr.	1·6 sp. gr.	1·7 sp. gr.
e at 1 inch =	0·00133	0·00150	0·00152
e „ 6 „ =	0·00855	0·00922	0·00973
e „ 11 „ =	0·01605	0·01728	0·01832

We learn from this the ratio in which e increases within limits seldom exceeded in practice. Thus we have

e at 6 inches of 1·5 sp. gr.	= 0·00855
„ 1 „ „ „	= 0·00133
Increase of e for 5 inches..	= 0·00722 consequently
„ „ 1 „ ..	= 0·00144

being the average expansion-coefficient for v for every inch from 1 to 6 inches.

In the same way are found the expansion-coefficients of the following table :—

Expansion co-efficients at 1·5 sp. gr.		at 1·6 sp. gr.	at 1·7 sp. gr.
From 1 to 6 inches . .	0·00144	0·00154	0·00164
„ 6 „ 11 „ . .	0·00150	0·00161	0·00172

Supposing we had read off 5·4 inches as the height of the acid, which was found to have a sp. gr. of about 1·6, we should have to make the correction by adding $5·4 \times 0·00154$, or 0·008316, to the 5·4 inches observed, as being the real height of the acid inside the chamber. The error consequently is so small that for low levels it may be altogether neglected, as well as the slight error arising from the loss of the small portion of acid which influences the average specific gravity.

Having described the nature of the instrument, I may now briefly explain how to use it. After having wetted the piston, which is necessary for its easy motion, it is pushed into the tube to a position high enough not to touch the level of the acid of which a sample is about to be taken. The pinch-cock is now removed, to open C D, and the instrument slowly lowered into the acid till it touches the bottom. After C D is closed again with the pinch-cock, the instrument has to be raised, and the level reached by the acid read off on the scale. On again opening the pinch-cock the acid will run out. This sample has to be rejected, having merely been drawn to ascertain approximatively the height of the level, in order to adjust the piston to its proper place, *i.e.*, 0·2 inches above the level. Before the next sample is drawn it will be well to blow through the piston-tube, in order to remove any portion of liquid which might have obstructed the passage. All the rest of the operation is then repeated as before, only with more care, especially in lowering the instrument with a slow, uniform, and perpendicular motion. After the acid adhering to the outside of A B has drained off, and the height of the level been read (the eye being carefully placed in a line with the surface), the pinch-cock is opened, the acid collected in a glass cylinder, and after mixture tested in the usual manner. When the acid in the chamber stands at a low level, it might be found troublesome to have to repeat the drawing of samples until a quantity of acid

is obtained, in which hydrometers of the usual size can float. This objection is easily met by employing smaller ones made on purpose.

Being now in possession of the means of ascertaining with accuracy the height and average specific gravity of the horizontal section of any liquid,* I may add a few words on the horizontal sections of the acid accumulating on the bottom of the chambers.

For reasons mentioned before, the sample has actually to be drawn from the inside of the chamber, which is generally effected by making a cavity of suitable dimensions in the side of the chamber, placed a foot or so above its bottom. A hole is provided in the bottom of this cavity for access to the acid underneath. If the bottom of the chamber be parallel with the surface of the acid, one determination is sufficient to fix the absolute weight of the whole. It will often happen, however, that, though the chambers were built level at first, they will in time become otherwise. If that is the case, one determination is insufficient, and the number and places of these determinations will depend upon the geometrical figure assumed by the vertical section of the acid. If the figure of this vertical section became too irregular, the task of fixing the accurate weight in this manner would have to be given up.

The heaviest acid will invariably gravitate to the lowest point in the chamber. Equal altitudes have equal gravities, and if samples drawn with the above instrument from the same chamber have different gravities, it is caused by irregularities in the level of the bottom.

Although the importance which is attached to these determinations lies less in the knowledge of the absolute weight of acid present at the time in the chamber, than in that of the exact quantity of acid which has been formed during a certain period, there is no possibility of knowing the one without the other. By fixing the level to-day and at the same point to-morrow, we learn from the altered height the volume formed in the interval, but not its weight, or at least only conditionally, that is, only under the assumption that the determinable part of acid, x , has

* The intimate mixture of large quantities of liquids demands considerable time and labour. As the average specific gravity after mixture is generally taken as the guide for fixing the desired proportion between two liquids to be mixed, numerous experimental mixtures and tests of the whole bulk may be avoided by the taking of samples with the above instrument.

the same specific gravity as the indeterminable part, y , and such might seldom be the case. If therefore y be of a higher specific gravity than x , x will become heavier at the expense of y , and we assume a greater yield of acid than we have actually made during the period in question. If y is weaker, the reverse takes place. The intervals between these determinations are generally so long, that the acid has to be removed from the chambers. In its further treatment it undergoes such a change that it becomes a homogeneous liquid, or a well-defined sulphate, in which state it is weighed. By this means all the errors arising from the heterogeneity of the acid are the more diminished the larger the proportion of homogeneous to heterogeneous acid. In other words, the longer those periods are, the nearer the calculation will come to the truth; on the other hand, the shorter they are, the more particular have we to be in all details which fix the weight.

XLIII.—*On some Products derived from Indigo-Blue.*

By EDWARD SCHUNCK, Ph.D., F.R.S.

[Abstract, from the third volume of the third series of Memoirs of the Literary and Philosophical Society of Manchester. Session 1864-5.]

My experiments on the formation of indigo-blue, an account of which I had the honour of presenting to this Society several years ago, led me to make some inquiries regarding the processes employed in tropical countries for the production of indigo from the various plants yielding that dye-stuff. I found that all the authors who have written on the subject agree in affirming that the process of fermentation, which is the one usually adopted for the purpose of extracting the colour from the plant, requires to be conducted with the greatest care, in order to yield a successful result. Unless certain precautions are adopted, a product of very inferior quality will be obtained; in some cases, indeed, the colouring matter is entirely lost. This will not be surprising to any one who considers that though indigo-blue, when once formed, is a very stable compound, the substance existing in the cells of the

plant from which it originates, and which I have named *indican*, is decomposed with the greatest facility in various ways; that indigo-blue is only one of its products of decomposition, and may be formed or not, according to the nature of the process to which it is submitted. With this sufficiently obvious explanation I should have been inclined to rest contented, had I not acquired a knowledge of some other facts relating to indigo-blue, to which the same explanation cannot be applied, but which evidently belong to the same class.

It is well known to those dyers who employ the so-called woad-vat, in which the reduction of the indigo-blue is effected by the action of various organic matters, such as woad, madder, and bran, together with lime, that if the process be not carefully managed it may change its character entirely, the contents of the vat entering into a state of complete putrefaction—a change which results in the total destruction, or at least disappearance, of the colouring matter. Now this phenomenon, the reality of which cannot be doubted, though its nature has never been subjected to scientific scrutiny, cannot be explained in accordance with what is at present known regarding indigo-blue, which is considered by chemists to be a body of such a stable character as not to be decomposed by any except very potent agents, such as chlorine, bromine, and nitric acid. In no work on scientific chemistry is it stated that indigo-blue may be decomposed by any process of fermentation or putrefaction, in the same way as sugar or albumen.

In my experiments on indigo-blue I have generally employed for its reduction and purification the process of Fritzsche, which consists in acting on it with a mixture of alcohol, grape-sugar, and caustic soda. The colouring matter dissolves when the mixture is heated, and is again deposited on exposure to the atmosphere in crystalline needles. Now in performing this operation with very small quantities of indigo-blue and an excess of alcohol and grape-sugar, I found that the colouring matter did not make its appearance again on agitating the solution with air. The yellow colour of the liquid passed as usual through red to green; but, instead of the indigo-blue being precipitated, the whole became yellow or brownish-yellow, and the colouring matter disappeared entirely. In this way I had the mortification of losing a quantity of indigo-blue, which I had prepared with much labour from human urine, though the loss resulted, as it afterwards turned out, in some gain of information.

This fact was also difficult to account for, since it is usually supposed that by the combined action of reducing agents and alkalies, indigo-blue merely takes up an atom of hydrogen and then dissolves, and, by the action of the atmospheric oxygen is again precipitated, unchanged, and undiminished in quantity.

In order to ascertain on what the disappearance of the colouring matter in this case depends, I first dissolved a small quantity of indigo-blue by means of grape-sugar and caustic soda, using water as a solvent instead of alcohol; but though the indigo-blue was kept for a long time in solution, and heat was applied at the same time to assist the action, it made its appearance again on exposure to the air, apparently undiminished in quantity. In another experiment, in which alcohol was used as the menstruum and protoxide of tin as the reducing agent, the same result was arrived at. It was therefore apparent that the disappearance of the colouring matter was due to the combined action of the alcohol and the grape-sugar, not to the separate action of either. By the use of a great excess of these two agents, together with caustic soda and the long-continued application of heat to the solution, I succeeded in causing several grammes of indigo-blue to disappear entirely. I avoid the word *decompose*, because, as I shall show, the colouring matter is not decomposed, but enters into new forms of combination.

It now occurred to me that since, by the action of caustic alkalies on sugar, acetic and formic acids are formed, the effect produced by the grape-sugar in this process might in reality be due to the presence of one or both of these acids rather than to that of the sugar itself. My supposition was completely verified by experiment. On treating some pure indigo-blue with alcohol, to which an alkaline solution of protoxide of tin was added until it dissolved, then adding acetate of soda and digesting at a moderate heat, the indigo-blue after some time ceased to be deposited on exposure to the air, or even agitation; it had entirely disappeared. The same thing occurred when formiate of soda was employed in the place of acetate. It was evident, therefore, that in this process acetic or formic acid was capable of playing the same part as grape-sugar; and as the use of the latter might have tended to introduce complications, in consequence of the formation of secondary products, I ceased to employ it in my subsequent experiments. The object of the present communication is to give an account of the combined action of alcohol, acetate of soda,

and caustic alkali on indigo-blue, and the products thereby formed.

At the commencement of the investigation I imagined that it was an essential condition that the indigo-blue should be in a state of solution; but I soon found that this was not necessary. The operation succeeds equally well if indigo-blue freshly precipitated or in fine powder be employed. The plan which I adopted was quite simple. Pure indigo-blue was introduced into a large quantity of ordinary spirits of wine, and the mixture, after being well agitated, was raised to the boiling-point. A quantity of pure acetate of soda previously deprived of its water of crystallisation, and a little solid caustic soda were then added, and the boiling was continued for several hours. A reduction of a portion of the indigo-blue took place in the first instance, as was evident from the deep red colour of the liquid. On agitating with air, this red colour disappeared for a moment, the indigo-blue being precipitated in powder, to be again dissolved on boiling the liquid; but after some time the liquid acquired a dark-brown colour, and deposited nothing on exposure or agitation. The process was then completed. There sometimes remained a residue of indigo-blue, which obstinately resisted the action of the boiling liquid; but, on pouring off the latter, and adding fresh materials, it generally disappeared rapidly. I found it advisable to employ only a small quantity of indigo-blue at a time, as the process is a slow one, and requires a great excess of alcohol and acetate of soda. The presence of caustic alkali I found to be quite essential, as no perceptible action took place without it; but the quantity required was not large. The stronger the alcohol, and, generally speaking, the freer from water all the substances employed were, the more rapidly was the process completed.

In order to obtain the products resulting from this process, I proceeded as follows:—The dark-brown alcoholic liquid containing them was first mixed with sulphuric acid until it had acquired a slightly acid reaction, and it was then evaporated. During evaporation, brown resinous masses were deposited; and on adding water, when the evaporation was nearly completed, a fresh quantity of resin-like matter was thrown down. The liquid filtered from this matter was still brown. It was evaporated to a syrup, which, after standing some time, became solid from the formation of crystals, consisting chiefly of acetate of soda. The whole mass of crystals was then dissolved in boiling alcohol, and tolerably

strong sulphuric acid was added to the solution, until no more sulphate of soda was precipitated, care being taken to avoid an excess of the acid. The liquid, after standing some time, was filtered and evaporated, so as to drive off the acetic acid as well as the alcohol. When the evaporation was nearly completed, water was added, which threw down a large quantity of a brown pulverulent substance, as well as a little brown resin, which, after filtration, were added to the resinous matter previously obtained. The filtered liquid had lost much of its brown colour. I shall return to it presently.

The products insoluble in water obtained in this manner consist partly of resinous, partly of pulverulent substances. Among these products there are at least five distinct substances, which I have succeeded in separating from one another by the use of various solvents; but it is probable that small quantities of other substances closely resembling them are also formed at the same time. Unfortunately, these bodies are all amorphous, and possess very few characteristic properties. It is indeed only their origin and mode of formation that impart to them any interest; and I shall therefore refrain from adding to the already cumbrous mass of terms with which organic chemistry has to deal by inventing names for them, but shall simply distinguish them by the letters of the alphabet.

The process adopted for the separation of these substances from one another was as follows:—The whole of the mass insoluble in water was first treated with boiling water in order to remove all the sulphate and acetate of soda. It was then dried, finely pounded, and treated with successive doses of ether, as long as anything dissolved. The ethereal liquid, which had a rich reddish-brown colour, was filtered and evaporated, when it left a resin-like residue of the same colour. This residue was digested with weak caustic ammonia, which dissolved a great portion of it. The portion insoluble in ammonia was filtered off, washed, dried, and then treated with ether, which generally left a small quantity of brown powder undissolved. The filtered ethereal solution was evaporated, and the residue was dissolved in cold alcohol, which left behind a little resinous matter. The filtered liquid left on evaporation a brittle, brownish-yellow resin, which I assume to be an unmixed substance, and shall distinguish by the letter A. The matter dissolved by the ammonia was precipitated by acid in thick flocks, which, after being filtered off, washed, and dried, were treated

with ether. The ether left some brown powder undissolved, which was separated by filtration. The liquid was evaporated, and the residue was again treated with ether, in order to separate a little more of the brown powder. The substance was then introduced into a hot solution of carbonate of ammonia, which, if not too concentrated, dissolved the greatest part of it, leaving only some brown powder behind. If, as sometimes happened, the solution of carbonate of ammonia was not sufficiently dilute, very little was dissolved by it, the greater part of the substance sinking to the bottom of the vessel as a viscid resinous mass, which dissolved however almost entirely on pouring off the liquid and adding pure water. The addition of acid to the filtered solution produced a brown flocculent precipitate, which was filtered off, washed with water, and treated with cold alcohol. The filtered alcoholic solution left, on evaporation, a resinous body hardly to be distinguished in appearance from the preceding; this I will denote by the letter B.

The matter insoluble in ether, constituting by far the larger part of the whole mass, was first treated with a little cold alcohol, to which it communicated a dark-brown colour. The filtered alcoholic liquid left, on evaporation, a brown resinous residue, which was not further examined, since it was sure to contain some of that well-known product of decomposition which is formed by the action of caustic fixed alkalies on alcohol, and which, being also resinous, I saw no prospect of being able to separate from any product derived from indigo-blue that might be mixed with it. The portion left undissolved by the cold alcohol was, after being dried, a brown powder, consisting of three substances. In order to separate these from one another, the mixture was first subjected to the action of boiling dilute caustic soda-lye, in which one of the three was found to be insoluble. The alkaline liquid, which was of a dark brown colour, was filtered, and the residue left undissolved was again treated with alkali in order to remove the whole of the soluble portion, and it was then treated with a boiling alcoholic solution of caustic soda, in which the greater part dissolved with ease. The dark-brown solution was filtered and then mixed with an excess of hydrochloric acid, which precipitated the greater part of the substance as a dark-brown powder. This was collected on a filter, washed with alcohol until the acid and chloride of sodium were removed, and dried. This body I will distinguish by the letter C. The caustic soda-lye

contained the two other substances in solution, and it was accordingly mixed with an excess of acid, which produced an abundant brown flocculent precipitate. This was collected on a filter, well washed with water, and then treated with a boiling solution of acetate of soda, which dissolved part of it, thereby acquiring a brown colour. The liquid was filtered boiling hot, and the residue was treated with fresh solution of acetate of soda, the process being repeated as long as the boiling liquid acquired any colour. The residue left undissolved by the acetate of soda was treated with boiling alcohol containing a little ammonia, in which it dissolved with ease, forming a dark-brown solution, from which the greatest part was again precipitated on the addition of an excess of hydrochloric acid as a brown powder. This was filtered off, well washed with alcohol, and dried. This body may be denoted by the letter D. The substance held in solution by the acetate of soda was precipitated by sulphuric acid in brown flocks, which were filtered off, well washed with water, and then treated with boiling alcohol, in which they dissolved completely. The alcoholic solution deposited, on cooling, a brown powder, which was collected on a filter, washed with a little cold alcohol, and dried. To this product I apply, for the sake of distinction, the letter E.

The acid liquid filtered from the mixture of substances insoluble in water still contained in solution a product of decomposition derived from the indigo-blue. It was evaporated until crystals began to appear on its surface, and was then set aside and allowed to stand for some time, when a large quantity of crystals was gradually deposited. After separation from the mother-liquor, these crystals appeared of a brown colour; but by recrystallisation from boiling water and decolorisation with animal charcoal, they were rendered white and pure. They were then found to have the properties and composition of anthranilic acid, the well-known product formed by the action of caustic alkalies on indigo-blue. The mother-liquor of the crystals left, on evaporation, a thick brown syrup, which seemed to be a compound of anthranilic acid and acetic acid. On dissolving it in water, adding sulphuric acid to the solution and evaporating, I obtained a quantity of crystals, which were purified by crystallisation, first from water, and then from boiling alcohol. They differed in appearance from anthranilic acid, and consisted indeed of a compound of the latter with sulphuric acid. The same compound is obtained

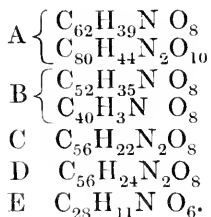
in place of uncombined anthranilic acid, if a great excess of sulphuric acid beyond what is required to unite with the free soda and that combined with acetic acid and the various products yielded by the process has been employed in the first instance. The sulphate, being more soluble in water than the free acid, does not crystallise so easily from the brown syrup which the liquid always leaves on evaporation, and hence it is advisable not to use an excess of sulphuric acid in the process above described for the separation of the anthranilic acid.

As regards their properties, the products insoluble in water present very little that is of interest. The body A is a brittle, amorphous, brownish-yellow resin, transparent in thin layers. At a temperature of 100° C. it becomes soft and semi-liquid. When heated on platinum foil, it burns with a bright flame, leaving much charcoal, which, on being heated, disappears without leaving any ash. It is decomposed by boiling nitric acid, yielding a product of decomposition in crystalline needles. It is quite insoluble in alkaline liquids, such as caustic potash, soda, and ammonia, even when a reducing agent, such as protoxide of tin, is added; but it is decomposed on being heated with dry soda-lime, giving off alkaline fumes having a peculiar penetrating odour. The body B can hardly be distinguished by its external appearance from A, with which it has also many properties in common; but it is easily soluble in caustic and carbonated alkalies, yielding yellow solutions, from which it is precipitated by acids in brown flocks. The compounds with baryta, lime, lead, silver, and copper prepared by double decomposition are brown or yellow, and insoluble in water. When treated with boiling nitric acid it behaves like A, yielding also a product of decomposition crystallising in needles. The body C is a brown powder, which, on being heated, burns without previously melting; it is insoluble, like A, in watery solutions of alkalies, and very little soluble in alcohol alone, but easily soluble in an alcoholic solution of soda. D resembles C in most of its properties, but differs from it by its solubility in caustic and carbonated alkalies. E is a reddish-brown powder, soluble in alkalies, and more easily soluble in alcohol than C and D, but distinguished from the others chiefly by its solubility in acetate of soda.

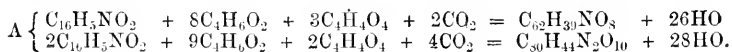
The composition of these bodies is, however, a matter of some interest, since it is only from a knowledge of their composition that any light can be thrown on the nature of this curious process.

I shall, therefore, proceed to give a short account of the results yielded by the analysis of these products, which will lead to a few remarks regarding their mode of formation and probable constitution.

From the results of their analyses, the following formulæ were respectively assigned to them :—



The compound D was formed in abundance, C and E in small quantities only. All the products were conceived to be produced by the combination of indigo, alcohol, and acetic acid, and in the case of A of carbonic acid (probably formed correlatively to the anthranilic acid), with elimination of water. To the specimens of A and B prepared at different times, though very similar in properties each to each, different formulæ had to be assigned, which, however, are derivable from similar modes of formation, thus :—



Anthranilic Acid.

Though there could be no doubt, after an examination of the properties of the crystallised acid formed in this process, of its identity with anthranilic acid, still I conceived that its analysis, if not altogether indispensable, might prove of some interest. The results obtained were as follows :—

I. 0.3135 grm., dried at 100° C., gave 0.7035 grm. carbonic acid and 0.1500 grm. water.

0.4050 grm., burnt with soda-lime, gave 0.2890 grm. metallic platinum.

II. 0.1664 grm. gave 0.3720 grm. carbonic acid and 0.0780 grm. water.

0.5590 grm. gave 49 cc. of moist nitrogen at 7° C. and 759.2 millims. pressure, equivalent to 47.25 cc. dry nitrogen at 0° C. and 760 millims. pressure, or 0.0591 grm.

These numbers correspond with the formula $C_{14}H_7NO_4$, which is that of anthranilic acid, as the following comparison of the composition with that required by theory will show:—

	Calculation.		Experiment.	
			I.	II.
C_{14}	84	61·31	61·19	60·97
H_7	7	5·10	5·31	5·20
N	14	10·21	10·13	10·58
O_4	32	23·38	23·37	23·25
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	137	100·00	100·00	100·00

Since, under ordinary circumstances, this acid can only be obtained by the long-continued action of boiling concentrated alkaline lye on indigo-blue, its formation in this process, in which only a small quantity of caustic soda dissolved in a large quantity of alcohol was employed, is remarkable. There can be little doubt that its formation in this case is connected in some way with that of the other substances, and could not be effected by the mere action of a dilute alcoholic solution of caustic alkali on indigo-blue.

The experiments just described suggest a few general remarks on this process and the products to which it gives rise.

1. Though I have no doubt that the products, of the properties and composition of which I have just given an account, are distinct chemical compounds, still it might be objected that some of them were not free from an admixture of products of decomposition derived from alcohol alone, the action of caustic alkali on alcohol being a process not very well understood. In order to satisfy myself on this point, I took an alcoholic solution of caustic soda, boiled it for some time, and then evaporated it in contact with the air. The solution became brown; and on adding water and an excess of acid, after evaporation of the alcohol, I obtained a brown flocculent precipitate, which, being filtered off and washed, was dissolved in alcohol. The solution left, on evaporation, a dark brown resinous residue, which I found to be quite insoluble in ether. That portion of the products obtained in this process which was insoluble in water and ether, but easily soluble in alcohol and alkalies, was therefore certain to contain some of this resinous matter; and I therefore laid the whole of it aside, and

gave up all further examination of it. It is certainly true that by the action of alkali on alcohol in closed vessels a totally different product is obtained—a product which differs from the other by its solubility in ether, and its total insolubility in alkalies, and shows a striking resemblance to the body A, which is also soluble in ether and insoluble in alkalies. Still, as my process was conducted in open vessels and not under pressure, I think it is not probable that any of this substance was formed.*

2. From what has been stated above, it follows that all the products, except anthranilic acid, are formed by a very simple process, which consists merely in indigo-blue combining with alcohol and acetic acid in various proportions, and yielding compounds in which none of the constituents as such can be detected. It is, therefore, not a process of decomposition, but rather a synthetical process, a building-up of complex bodies from others of a simpler constitution. This is proved by the fact of water being eliminated during the process, whereas in all cases in which complex organic substances are decomposed into simpler ones, water is absorbed. This elimination of water proceeds so far, that some of the products, notwithstanding that they are formed by the addition to indigo-blue of many atoms of alcohol and acetic acid (bodies having much less carbon and more oxygen), are found to contain even more carbon than indigo-blue itself, a great proportion of the water, both of the alcohol and the acetic acid, having been separated. Is it not possible that processes of a similar nature may go on within the cells of plants, the chief function of which

* According to Liebig, the colour which an alcoholic solution of caustic potash assumes in contact with the air is due to aldehyde-resin, the product of decomposition formed by the action of caustic alkalies on aldehyde. Weidenbusch (*Ann. Ch. Pharm.* lxi, S. 153), however, states that the true aldehyde-resin is almost insoluble in alkalies; and in consequence of the discrepancy in the accounts of this body, I requested Mr. A. Mylius to make some experiments on the action of caustic alkalies on alcohol in sealed tubes. He obtained by this action a resin of a fine reddish-yellow colour, soluble in ether, but totally insoluble in watery solutions of alkalies. Its properties so nearly resemble those of the true aldehyde-resin, as described by Weidenbusch, and its composition differs so little from that of the latter, that it seems very probable that the two resins may be identical. If so, it follows that aldehyde-resin is certainly formed by the action of caustic alkalies on alcohol, but only under pressure in sealed tubes. The resin formed in open vessels in contact with the air is totally different. For further particulars regarding this peculiar action, I must refer to the account of Mr. Mylius's experiments contained in the Proceedings of the Manchester Literary and Philosophical Society, February 21st, 1865.

is known to consist, chemically speaking, in the construction of complex bodies from others of a simpler composition? Is not the power residing in the vegetable cell which enables it to neutralise very potent chemical affinities somewhat of the same nature as that which, in this process, causes the acetic acid to leave the strong base with which it is combined in order to unite with alcohol and indigo-blue, for which it cannot be supposed to have any strong chemical affinity?

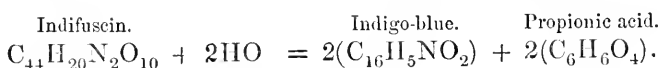
3. The physical properties of these compounds do not seem to depend in any way on those of their constituents. Nevertheless it is to be observed that those containing the largest proportion of alcohol are insoluble in alkalies, whilst those in which the indigo-blue preponderates are the least soluble in alcohol and ether.

4. No law or rule can be detected determining the number of atoms of alcohol and acetic acid which are capable of uniting with the indigo-blue. Were the series more extensive, it is probable that some such law might be found to prevail. It may be remarked, however, that all the products insoluble in water, with one exception, contain either 8 or 10 equivalents of oxygen.

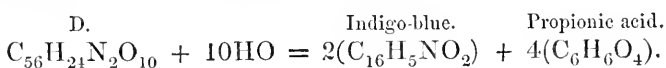
5. Regarding the rational formulæ or probable internal constitution of these compounds I hardly venture to indulge in any speculations. They might be considered as conjugated compounds—compounds of which organic chemistry affords so many examples; and it might consequently be possible to obtain from them, by decomposition, some of the simpler bodies which are known to have entered into their composition. I have, however, been unable to discover any facts in favour of this view. Neither indigo-blue nor any of its products of decomposition can be obtained from them by any means which I have tried.

In this respect these compounds resemble some of the secondary products which are formed during the decomposition of indican by acids, and from which no indigo-blue can be obtained, though they must be supposed to contain the elements of that body and of various organic acids, such as formic, acetic, and propionic acids. Indeed, the resemblance between the two series of compounds extends also to their physical properties. For instance, the body A resembles indifulvin, one of the products derived from indican, both being brownish-yellow resins insoluble in alkalies. B is very

similar to indiretin; and D is so like indifuscin, that the two can hardly be distinguished from one another. There may, in fact, be some analogy in the composition of the two last-named bodies. Indifuscin may, as I have shown on a former occasion, be considered as a compound of indigo-blue and propionic acid minus water, as may be seen by the following equation:—

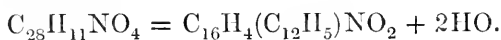


In like manner D may be supposed to contain the same elements combined in a different proportion, since



Analogies such as these, unsupported by experimental proof, may be only fanciful. Nevertheless they may prove of some use in facilitating the classification of facts. At all events, the circumstance of indigo-blue yielding, by the combined action of alcohol, acetic acid, and alkalis, bodies so closely resembling the products obtained along with indigo-blue in the decomposition of indican seems to afford a striking confirmation of the view which I have taken regarding the composition of these products.

There is another point of view from which these bodies may be considered. They may be represented as substitution products of indigo-blue, one or more of the atoms of hydrogen in the latter being replaced by one or more organic radicals. For instance, the body C may be looked upon as the hydrate of a compound, in which one atom of the hydrogen of indigo-blue is replaced by phenyl (C_{12}H_5), since



In order to obtain some confirmation of this hypothesis, I took some of the body D, of which I had a considerable quantity, and which differs from C only by containing more water, and subjected it to the action of hydriodic acid and phosphorus in a sealed tube. By the action of the nascent hydrogen I expected that indigo-blue might possibly be regenerated, but the experiment led only to a negative result; for though the tube was heated in the water-bath for several days, the substance, on its being opened, was found to be almost unchanged, a small part only having been con-

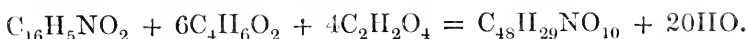
verted into a resinous matter easily soluble in alcohol. A similar negative result was obtained when an amalgam of sodium was employed as a source of hydrogen. After these failures I felt but little encouragement in making further experiments in this direction; and this part of the subject must, therefore, be left in its present state of obscurity.

6. The occasional disappearance of the indigo-blue in the woadvat, in consequence of mismanagement, now admits of an explanation, which will probably be allowed to be the correct one. By the fermentation of the sugar contained in the madder and other materials employed, alcohol is generated, which in its turn may yield some acetic acid; and alcohol, acetic acid, and a base (lime) being present, nothing further is required for the development of the process above described. By neutralizing a portion of the lime when necessary, the danger of losing colouring matter is to some extent obviated; but I would venture to suggest, as a means of rendering it still less, the avoiding all materials containing much sugar or starch—substances which might, by their decomposition, lead to the formation of alcohol.

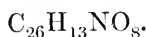
When, in the process above described, formiate of soda is employed instead of acetate of soda, exactly the same phenomena are observed. The indigo-blue gradually disappears, and a dark brown alcoholic liquid is obtained, which is found to contain bodies closely resembling those formed by means of acetate of soda. By operating on a tolerably large quantity of material, I was enabled to ascertain the presence in this liquid of anthranilic acid, and of three products corresponding to, and having the same physical properties as, the bodies B, D, and E. They were separated from one another by the same means as the latter, the first being a brownish-yellow resin, easily soluble in alcohol and ether, as well as in alkalies; the second, a brown powder, soluble in alkalies, but soluble with difficulty in alcohol and ether; whilst the third was a reddish-brown powder, distinguished by its solubility in a boiling solution of acetate of soda—a property which afforded a ready means of separating it from the others. No compounds insoluble in alkalies, and corresponding to the bodies A and C, were produced with formiate of soda. The analysis of the compound resembling B led to the formula $C_{48}H_{29}NO_{10}$.

		Calculation.	Experiment.
C ₄₈	288	70·07	69·70
H ₂₉	29	7·05	7·20
N	14	3·40	3·32
O ₁₀	80	19·48	19·78
	<hr/> 411	<hr/> 100·00	<hr/> 100·00

Its formation may be represented by the equation :

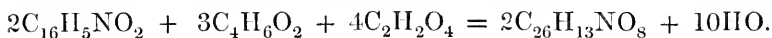


The analysis of the substance corresponding to E, yielded numbers which may be approximately represented by the formula,



		Calculation.	Experiment.
C ₂₆	156	63·15	62·61
H ₁₃	13	5·26	4·64
N	14	5·66	5·61
O ₈	64	25·93	27·14
	<hr/> 247	<hr/> 100·00	<hr/> 100·00

Assuming this to be the correct formula, the formation of the compound may be represented by the equation :—



It will be seen that the same law regarding the number of atoms of oxygen prevails here as in the case of the bodies before described, this number being either 8 or 10.

If in this process ordinary alcohol is replaced by methylic alcohol, the same effect is produced, provided acetate of soda is employed ; but a mixture of methylic alcohol, formiate of soda, and caustic soda does not act in the same manner on indigo-blue, which remains unchanged, however long it may be left in contact with the boiling liquid. It appears, therefore, that one of the two agents, ethylic alcohol or acetic acid, is quite essential. One of the two may be replaced by an homologous body ; but when both are so replaced, the indigo-blue remains intact.

[Contributions from the Laboratory of the London Institution]

XLIV.—*The Relation between the Products of gradual Oxidation and the Molecular Constitution of the Bodies Oxidised.*

By ERNEST THEOPHRON CHAPMAN and WILLIAM THORP.

WE believe it will be generally allowed that the greatest problem now occupying the attention of chemists is that of isomerism. There are two methods by which this problem may be attacked. We may either synthetically form the isomeric compounds and compare them, or we may decompose the already formed isomeric compounds into their proximate constituents. The first method requires assistance from the second, because, as isomeric bodies frequently have almost identical physical properties, a difficulty may arise in determining whether such bodies are not really identical, and not only isomeric. All tests, such as the boiling-point, fusing-point, &c., are liable to be rendered fallacious by the presence of traces of foreign matter. We therefore require a method by which we may determine what are the proximate constituents of isomeric bodies. We believe that gradual oxidation fulfils this requirement. But before adopting this method, it is requisite to examine its action on bodies, the molecular grouping of which is well understood, and also on those products which may be termed proximate oxidation-products, more particularly the acids of the acetic series. We have made such an examination, and though at present it has been confined to substances connected with the vinic series, it has led us to the conclusion that, by the gradual oxidation of complex organic molecules, simpler groups are produced; that these simpler groups represent the radicles entering into the composition of the substances oxidized; and, finally, that these representative groups themselves can only with great difficulty be further oxidized.

1. All bodies derived from the vinic series, that we have yet oxidized, have yielded acids of the acetic series, and in some instances carbonic acid. The first step, therefore, in this investigation is to examine the action of oxidizing agents on this class of

acids. With this object, three solutions were prepared, containing respectively 3, 5, and 8 per cent. of bi-chromate of potash. They were prepared by dissolving the requisite quantity of bichromate of potash in water, and adding sufficient sulphuric acid to combine with the potash as bi-sulphate, and with the chromium as sulphate of sesquioxide. To these solutions small quantities of pure acetic acid were added, the mixtures sealed up in digestion-tubes, and heated for twelve hours in the water-bath. On examining the tubes, the 3 and 5 per cent. solutions had not sensibly altered their colour, the 8 per cent. had slightly changed, but no gas was evolved on opening any of them. All three tubes were sealed up again and heated as before for 24 hours, along with a similar tube containing the 8 per cent. mixture without acetic acid; at the end of this period the contents of the tubes had slightly altered in colour, though not perceptibly more so than the tube containing no acetic acid; still little or no gas was evolved. All four tubes were now heated for four hours to 130° C.; on opening, gas escaped from all four, though only in minute quantities from the 3 and 5 per cent. tubes; both the 8 per cent. tubes yielded rather more. The gas from the 8 per cent. tube containing acetic acid was tested for carbonic acid, of which it contained a small quantity. The contents of all three tubes were now distilled, the distillates boiled with excess of carbonate of baryta, filtered, evaporated on the water-bath, and the percentages of barium determined. The results were as follows :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
(1) 0·4366	0·3978	53·57	53·726	Acetic acid
(2) 0·2984	0·2720	53·60	"	" "
(3) 0·3308	0·3015	53·59	"	" "
(4) 0·4082	0·3718	53·55	"	" "
(5) 0·3464	0·3154	53·54	"	" "
(6) 0·4658	0·4272	53·58	"	" "

Numbers 1 and 2 are from the 3 per cent. tube.

" 3 " 4 " 5 "

" 5 " 6 " 8 "

From the foregoing determinations it is evident that acetic acid withstands the action of this oxidizing agent very perfectly.

2. Propionic acid was the next member of this series experimented upon. It was prepared from cyanide of ethyl. It was heated with the 5 per cent. mixture for 24 hours at 100° C. The contents of the tube were diluted and distilled—diluted because the boiling-point of the mixture is considerably above that of water; therefore had this been omitted, the experiment would not have been a fair one. The distillate (free from sulphuric acid) was neutralised with standard solution of potash, enough sulphuric acid added to combine with two-thirds of the potash, the mixture distilled, the distillate converted into a baryta-salt, and the percentage of barium determined.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
0·4032	0·3306	48·22	48·41	Propionic acid
0·4648	0·3815	48·27	„	„ „

This fraction of the propionic acid was, therefore, unaltered.

Now if any acetic acid whatsoever were produced, it would remain in combination with the potash in the retort; excess of sulphuric acid was, therefore, added to the contents of the retort and those contents distilled; the distillate, as before, was converted into a baryta-salt, and the percentage of barium determined.

Substance taken.	Ba ₂ SO ₄	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds
0·3975	0·3266	48·33	48·41	Propionic acid
0·3624	0·2976	48·28	„	„ „

These numbers prove the absence of acetic acid. There can, therefore, be no doubt that propionic acid also will endure long-continued digestion with dilute chromic acid at 100° C.; at a higher temperature, however, propionic acid is easily decomposed by oxidizing agents. Four hours' digestion with an 8 per cent. solution of chromic acid at 130° C. is sufficient to cause a large evolution of carbonic acid.*

* In the oxidation of this ketone from carbonic oxide and sodium-ethyl, Wanklyn

3. Valerianic acid was next subjected to the action of oxidizing agents. Like the preceding acid it withstands their action at the temperature of boiling water, but at 130° C. is pretty rapidly decomposed. As in the case of acetic acid, three simultaneous experiments were made with 3, 5, and 8 per cent. solutions, the digestion being continued for twelve hours in the water-bath. The 3 and 5 per cent. tubes yielded no gas on opening, the 8 per cent. gave forth a little. The contents of all three tubes were diluted and distilled, and the distillates from the 3 and 5 per cent. tubes were at once converted into baryta-salts. The distillate from the 8 per cent. tube was neutralised with standard solution of caustic potash, and divided into three fractions by the addition of the necessary quantity of sulphuric acid, and by distillation. The first and third fractions were converted into baryta-salts. The following table contains the percentages of barium* in these salts, and also in the salts from the 3 and 5 per cent. tubes :—

Substance taken.	Ba ₃ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which it corresponds.
From 3 per cent. tube				
0·3608	0·2457	40·05	40·413	Valerianic acid
0·4114	0·2808	40·13	„	„
From 5 per cent. tube				
0·2998	0·2044	40·09	„	„
0·3670	0·2504	40·11	„	„
8 per cent. tube 1st frac.				
0·3938	0·2694	40·21	„	„
0·3078	0·2102	40·16	„	„
0·4654 2nd frac.	0·2773	40·22	„	„
0·3726	0·2548	40·21	„	„

From this table it appears that the above treatment had not affected valerianic acid.†

heated this substance, which yields acetic acid and propionic acid, for many hours in a digestion tube, together with excess of bichromate of potash and dilute sulphuric acid. No carbonic acid was formed, thereby proving that in this experiment neither acid had undergone decomposition.—(Chem. Soc. J., August, 1866, page 326 of this volume.)

* In this table the barium was determined as sulphate by precipitation.

† One sample of this acid was found to decompose on treatment like that described in the text; it decomposed readily, and produced butyric and carbonic acids. The acid which split up in this way was furnished by one of the London druggists, but we could not learn its history; it could not have been a primary acid.

4. Lastly, caproic acid was submitted to the action of oxidizing agents. Two samples of this acid were employed, the one obtained from cyanide of amyl, the other from a ketone obtained by the distillation of ricinolate of potash; this ketone, when oxidized, yields caproic and carbonic acids. Both these samples were exposed to the action of 5 per cent. chromic acid solution for twelve hours, at the temperature of the water-bath; neither underwent any perceptible change, though in both instances the bichromate was slightly discoloured. Both samples were separated by distillation from the chromic acid and converted into baryta-salts. Determinations 1 and 2, in the following table, are from the caproic acid prepared from cyanide of amyl; 3 and 4 from the other sample.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
(1) 0·4444	0·2824	37·37	37·33	Caproic acid
(2) 0·3886	0·2472	37·48	"	" "
(3) 0·4306	0·2728	37·25	"	" "
(4) 0·3946	0·2497	37·21	"	" "

It is perhaps worth while to remark that, in converting the higher acids into baryta-salts, hydrate of baryta is preferable to the carbonate.

The action of dilute permanganic acid was then investigated. This substance, when dilute, has little or no action on acetic and propionic acids, even when boiled with them. In its concentrated state, however, it decomposes them pretty rapidly. But as it was not our intention to work with this substance, we did not further investigate its action on the acids of the acetic series.

We think we are justified by the above experiments in our statement that, under ordinary circumstances, and at the temperature of the water-bath, these acids are not attacked by dilute chromic acid.

We will now mention a few exceptional circumstances which have great effect on the rapidity of the action of chromic acid. The following circumstances promote the action:—

1st. Presence of large excess of concentrated sulphuric acid.

2nd. Presence of free chromic acid, *i.e.*, chromic acid that has been actually separated from potash.

3rd. Presence of a very small quantity of binoxide of manganese.

In the first case it is to be observed that acetic and propionic acids are not affected by the excess of sulphuric acid, unless this be so great as to develop heat on mixing with water. We are unable to account for the more violent action in the second and third cases.

On the other hand, if we substitute phosphoric for sulphuric acid, we obtain an oxidizing mixture which appears to be absolutely without action upon the acids of this series, though it is quite capable of oxidizing alcohol, &c.

Having now proved that, if the acids of this series be once formed by oxidation they are not destroyed by excess of the oxidizing agent, we are in a position to observe the effects of this oxidation on a series of compounds, the molecular constitution of which is well understood. The substances selected for this series of experiments were the following:—

- | | | |
|------------------------|-------------------------|-----------------|
| 1. Ethyl-alcohol | 7. Nitrite of amyl | 13. Ethylamine |
| 2. Amyl-alcohol | 8. Nitrate of ethyl | 14. Propylamine |
| 3. Acetate of ethyl | 9. Nitrate of methyl | 15. Amylamine |
| 4. Acetate of methyl | 10. Iodide of ethyl | 16. Ethyl-amyl- |
| 5. Acetate of amyl | 11. Iodide of amyl | amine |
| 6. Valerianate of amyl | 12. Iodide of isopropyl | |

We will call the products obtained by carrying this oxidation as far as we can without endangering the acids produced, *proximate* oxidation-products; and those obtained either by limiting the period of action or employing an insufficient quantity of the oxidizing agent, *mediate* products.

1. *Ethyl-alcohol*.—In the first place it was necessary to obtain chemically pure alcohol. The test employed to determine its purity was to oxidize a portion of it with excess of chromic acid, distil off the acids formed, *nearly* neutralize the distillate with potash and distil again, carrying the distillation to dryness. As all the acids of the acetic series, at any rate all the lower members of that series, are expelled from their compounds by acetic acid, it follows that, had any homologues of alcohol been present, they would, by their oxidation, have furnished acids differing from acetic acid in their saturating capacity, and that these acids would

all accumulate in the small fraction described above. When, therefore, a sample of alcohol, yielded nothing but acetic acid by this treatment, it was obviously free from homologues; and as it had previously been digested with caustic potash, it must also have been free from compound ethers. It was oxidized with chromic acid in insufficient quantity to produce the proximate products of oxidation; aldehyde and acetic acid were obtained, and also a neutral liquid not completely miscible with water, and smelling of acetic ether. It was digested with potash, excess of sulphuric acid added, and the acid thus liberated distilled off: it proved to be pure acetic acid. Another portion of the alcohol was heated with excess of chromic acid in a sealed tube for about three hours; the contents of the tube were distilled, and the distillate examined by Liebig's method for fractionating acids. We could detect no product excepting acetic acid.

2. *Amyl-alcohol*.—A portion of this alcohol was digested with 5 per cent. solution of chromic acid for one hour; the contents of the tube were distilled; and the distillate saturated with sulphate of soda, whereby the oily layer on its surface was greatly augmented; this oily layer was decanted, distilled, and treated with solution of carbonate of soda, whereby a portion was dissolved. The remainder (supposed to be a compound ether) was decanted and digested with alcoholic solution of potash. It was then treated with excess of sulphuric acid and distilled. The solution in carbonate of soda was treated in the same manner. The original distillate, which had been saturated with sulphate of soda, was re-distilled; all three distillates gave an acid reaction, and smelt and tasted of valerianic acid. They were converted into baryta-salts; the percentages of barium obtained from them are tabulated below. Another sample of the amyl-alcohol was digested for six or seven hours with 5 per cent. chromic acid solution; no gas was evolved. The contents of the tube were diluted and distilled; the distillate, which was totally soluble in alkalis, divided into three fractions by Liebig's method, and the first and third fractions converted into baryta-salts; the percentages of barium obtained from these salts will be found on the next page.

As will be seen, the whole of the above percentages correspond to valerianic acid.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
(1) Free acid— 0 5782	0 3960	40 27	40 413	Valerianic acid
(2) Free acid remaining in distillate— 0 4362	0 2991	40 32	"	" "
(3) Acid from ether - 0 3774 0 3814	0 2588 0 2620	40 32 40 38	" "	" " "
(4) First fraction— 0 2998 0 3228	0 2053 0 2215	40 27 40 35	" "	" " "
(5) Second fraction— 0 3436	0 2353	40 27	"	" "

The first oxidation of both the foregoing alcohols produced a complicated result. In both the corresponding aldehyde was no doubt formed, in both we had a compound ether formed, and in both we had the acids formed. As will be seen below, we have proved that these two compound ethers—acetate of ethyl and valerianate of amyl—yield, the one nothing but acetic acid, the other nothing but valerianic acid, when oxidized. Therefore, the apparent complication of the products has in reality no effect on the ultimate result.

3. *Acetate of Ethyl*.—This compound was oxidised both with chromic and permanganic acids; by the former at the boiling-point of water, by the latter both in the cold and at the boiling-point. The products of all three operations were separately distilled, and each of the three converted into baryta-salts; the percentages of barium obtained from these salts will be found in the annexed table, all corresponding to acetic acid.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
Chromic acid— 0 4264 0 3712	0 3885 0 3384	53 64 53 67	53 726 "	Acetic acid " "
Permanganic acid, hot— 0 4212	0 3846	53 70	"	" "
Permanganic acid, cold— 0 3455	0 3153	53 66	"	" "

4. *Acetate of Methyl*.—This compound was oxidised with chromic acid; it yielded acetic and carbonic acids. Formic acid also was tested for and found, though the greater proportion of this acid had evidently split up into carbonic acid and water.

5. *Acetate of Amyl*.—This compound is not very easy to oxidize, requiring several hours' heating in the water-bath, with five per cent. chromic acid solution. If it be imperfectly oxidized, valerianic aldehyde is apparently formed. If, however, the oxidation be carried far enough, acetic and valerianic acids only are produced. This was proved by diluting the contents of the digestion tube, distilling, dividing the distillate into three fractions by Liebig's method, converting the first and last fractions into baryta-salts, and determining the percentages of barium. They corresponded, the first to valerianate, the second to acetate, as will be seen in the next table :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction —				
0·4416	0·3029	40·33	40·413	Valerianic acid
0·4764	0·3258	40·21	”	” ”
Third fraction —				
0·4145	0·3768	53·46	53·726	Acetic acid
0·3624	0·3297	53·49	”	” ”

6. *Valerianate of Amyl*.—This substance is even more difficult to oxidize than the corresponding acetate. It will not bear a temperature much higher than 100° C., nor the action of a very concentrated solution of chromic acid. However, by using a great excess of dilute chromic acid, the oxidation was effected pretty easily. On distillation and fractionation of the distillate by Liebig's method, it became evident that we were dealing with valerianic acid. The first and last fractions were converted into baryta-salts and the percentages of barium obtained, which we give in the annexed table :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·4286	0·2938	40·30	40·413	Valerianic acid
0·3578	0·2454	40·33	„	„ „
Third fraction— 0·3582	0·2454	40·28	„	„ „

These numbers all correspond to valerianic acid.

7. *Nitrite of Amyl*.—This substance, as elsewhere shown,* yields, by oxidation, nitric and valerianic acids, and, if the oxidation be incomplete, valerianate of amyl.

8. *Nitrate of Ethyl*.—By oxidation this compound yields nitric and acetic acids.

9. *Nitrate of Methyl*.—From this substance we obtain nitric and carbonic acids by oxidation.

10. *Iodide of Ethyl*.—This compound oxidizes without difficulty. Iodine is liberated in abundance during the digestion. The contents of the digestion-tube were diluted and distilled, the distillate treated with mercury to remove the iodine, redistilled, and divided into three fractions. The first and last fractions were converted into baryta-salts, and the percentages of barium in the annexed statement obtained from them:—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·3989	0·3637	53·61	53·726	Acetic acid
Third fraction— 0·3838	0·3500	53·62	„	„ „

Both corresponding to acetic acid.

11. *Iodide of Amyl*.—This compound is somewhat difficult to oxidize; nevertheless, by treatment similar to that described in the last paragraph, it was made to yield an acid. This acid, when

freed from iodine. was found to be pure valerianic acid. This was proved by dividing it into three fractions, and converting the first and third into baryta-salts; from these salts the annexed numbers were obtained :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·4226 0·4074	0·2899 0·2796	40·34 40·36	40·413 "	Valerianic acid " "
Third fraction— 0·2788	0·1918	40·45	"	" "

12. *Iodide of Isopropyl*.—This substance yielded much gas during its oxidation, which proved to be carbonic acid. The contents of the digestion-tube were treated as in the case of iodide of ethyl, the first and last fractions so obtained were converted into baryta-salts, and, as will be seen from the annexed barium determinations, were nothing but pure acetic acid :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·3570	0·3249	53·51	53·726	Acetic acid
Third fraction— 0·3672	0·3349	53·63	"	" "

13. *Ethylamine*.—It has already been proved that this compound yields, by oxidation, acetic acid.*

14. *Propylamine*.—We know that isopropyl compounds do not yield propionic acid by oxidation, also that it is possible to prepare a propyl compound, viz., propylamine. Now it is probable that we shall ultimately succeed in converting the alcoholic ammonias into the corresponding alcohols, and thus effect the ascent of the alcohol series. This being the case, it was obviously most important to determine whether the propylamine obtained from

* Wanklyn and Chapman, Chem. Soc. J., August, 1866.

cyanide of ethyl was a primary or a secondary compound. If the method of investigation, above described, be of any value, it would decide this question at once. We have, therefore, oxidized propylamine. The experiment was carried on in a digestion-tube, with three per cent. chromic acid solution, at a temperature of 100° C. When the digestion was complete, the tube was opened, the escaping gas being collected over mercury. Not the slightest absorption occurred on the introduction of potash into this gas, thus proving the absence of carbonic acid. The contents of the digestion-tube were diluted, and the acid formed was distilled off. It was converted into a baryta-salt; the following table contains the percentages obtained from it, all corresponding to propionate :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
0.5072	0.4166	48.29	48.41	Propionic acid
0.3238	0.2656	48.23		

15. *Amylamine*.—The oxidation of this substance requires care; it is not very easily or rather not very rapidly effected. We found that the quickest way to oxidize it, was to treat it with concentrated chromic acid, but at a temperature not higher than 70° or 80° C. After half an hour of this treatment, the fluid was diluted and the digestion continued at the temperature of the water-bath. The first treatment with concentrated acid appears to start the reaction, after which the dilute acid easily completes it. Much time is saved by this method of treatment, both in this and the following case. The acid formed was distilled off and converted into a baryta-salt, which yielded the following numbers, corresponding to valerianate :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
0.4056	0.2784	40.35	40.413	Valerianic acid
0.2602	0.1824	40.29		

16. *Ethyl-amylamine*.—This compound is more rapidly attacked, though it takes a long time to complete the re-action. The products of the digestion were diluted, distilled, and fractionated, and the first and last fractions converted into baryta-salts, from which the following percentages were obtained. They correspond to valerianic and acetic acids :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·3824	0·2619	40·29	40·413	Valerianic acid
0·3266	0·2240	40·32	„	
Last fraction— 0·4338	0·3945	53·47	53·726	Acetic acid

Observations.—The whole of the foregoing oxidations were conducted in sealed digestion-tubes, and in no instance was the temperature employed higher than that of boiling water, generally from 10° to 20° below it. With the exception of the last two oxidations, the chromic acid employed was in no instance stronger than 8 per cent., and generally less than 5 per cent. Nearly all these experiments have been repeated twice, and some of them three times. The greatest possible care was taken to obtain pure substances. The four compound ethers—acetate of ethyl, acetate of methyl, acetate of amyl, and valerianate of amyl—were all titrated, *i.e.* the percentage of acid which they yielded to caustic potash determined, which, it is obvious, is a complete guarantee of their purity. The acetate of amyl, and valerianate of amyl, were obtained by acting with iodide of amyl on acetate and valerianate of potash. The object in adopting this method of preparation was to eliminate any possible action of sulphuric acid on the molecular arrangement of the alcohol in question.

The fractionations were performed in the following manner:—The contents of the digestion tube having been diluted and distilled, the distillate was tested for sulphuric acid, which was invariably found to be absent when the distillation had been carefully conducted. It was then neutralized with standard solution of caustic potash, and sufficient standard sulphuric acid added to

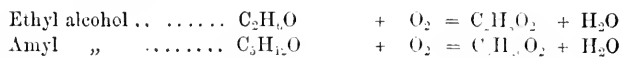
combine with a third of the potash employed, thereby liberating an equivalent third of the acids operated upon. The liberated acid was then distilled off, a sample of it converted into a baryta-salt, and the percentage of barium in this salt determined. If it corresponded to any one of the acids of the acetic series, we proceeded no further with this fraction. If it did not, but differed considerably from any known member of the series, the process was repeated. This was, however, hardly ever requisite, as, from the nature of the substances operated on, we never had occasion to separate any acids excepting acetic and valerianic acids, and in that case the valerianic acid generally distils over in the first fraction in a state of perfect purity. A second third of sulphuric acid was now added to the original distillate, and the acid thereby liberated distilled off. Excess of acid was employed to obtain the third fraction, and this third fraction treated in precisely the same manner as the first. If the percentages obtained from the first and third fractions corresponded, it was obvious that we were dealing with a single acid, and therefore it was unnecessary to examine the second fraction. If, however, they differed, the second fraction was always examined, though we have not thought it necessary to give the details of these examinations.

The barium was, unless otherwise stated, determined as sulphate by heating the dry salt with concentrated sulphuric acid. This method is exceedingly rapid, and perhaps the most accurate known.

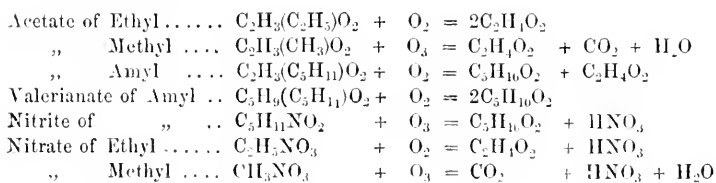
The annexed table will show precisely the nature of the results obtained in the foregoing portion of this paper:—

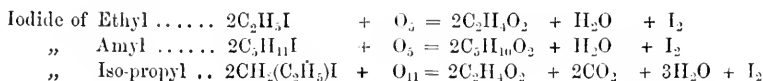
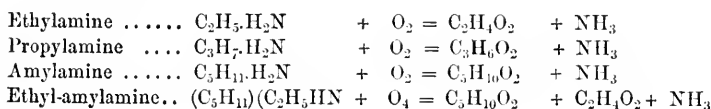
Table showing the proximate oxidation products of the following substances.

Alcohols.



Compound Ethers.



Iodides of Alcohol-radicles.*Ammonia-bases.*

The first application made by us of the knowledge acquired by the foregoing experiments was the oxidation of certain of the olefines, an account of which was read at the Nottingham meeting of the British Association.

Ethylene.—This substance is not easy to oxidise by the action of dilute chromic acid, but it yields without difficulty to hot concentrated solutions. The results are carbonic acid and water. We could not detect formic acid.

Amylene.—This substance was digested for many hours with a moderately concentrated solution of chromic acid. When the amylene had disappeared, the contents of the tube were diluted, distilled, and fractionated, the first and last fraction converted into baryta salts, from which the following percentages were obtained:—

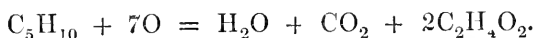
Substance taken.	BaSO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction—				
0·4826	0·4318	52·61	53·726	Acetic acid
0·3014	0·2720	52·67	”	” ”
Third fraction—				
0·6089	0·5566	53·75		

These numbers show that the substance in hand is acetic acid.

The determinations in fraction 1 are slightly too low. This is due, without question, to a trace of impurity in the substance employed. Carbonic acid was evolved in abundance during the oxidation. In an experiment made to determine the amount of acid produced from amylene by oxidation, 4 grm. of amylene yielded 6·12 of acetic acid, or 153 per cent. If 1 eq. of amylene

yields 2 eqs. of acetic acid, the percentage should have been 171·4. It yielded, therefore, 89·3 per cent. of the theoretical quantity. Now, as the tube had been opened to allow of the escape of carbonic acid, and as, therefore, some amylene was without doubt lost, this is quite sufficiently near to prove our point, viz., that 2 eqs. of acetic acid are formed.

The above work was repeated under circumstances the most varied as to concentration of chromic acid, &c., but always with the same result. Acid solution of permanganate produced the same result, no matter whether used cold or hot. The decomposition of amylene, therefore, by nascent oxygen, is as follows:—



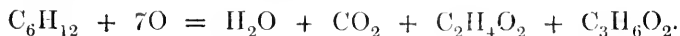
β-Hexylene.—Four grammes of this substance were digested with moderately dilute solution of chromic acid in the water-bath. The tube was cooled, and opened to allow the escape of gas (carbonic acid) twice. When the digestion was completed, the contents of the tube were diluted and distilled. The distillate was free from sulphuric acid. It was neutralised with standard solution of potash, of which it required a quantity corresponding to 3·16 grammes of potassium. Had it yielded 2 eqs. of acid, it would have required 3·815. It, therefore, yielded 82 per cent. of the required quantity, which, considering the loss which must have occurred when the tube was opened, is a sufficiently close approximation.

The acids combined with the potash were now submitted to fractionation, the fractions converted into baryta-salts, and the percentage of barium determined:—

Substance taken.	Ba SO ₄ found.	Per cent. Ba found	The retical per cent.	Acid to which this corresponds.
First fraction— 0·3140 0·3336	0·2577 0·2734	48·26 48·19	48·41	Propionic acid
Second fraction— 0·3745	0·3144	49·36	intermediate	
Third fraction— 0·4555 0·4998	0·4159 0·4569	53·68 53·75	53·726	Acetic acid

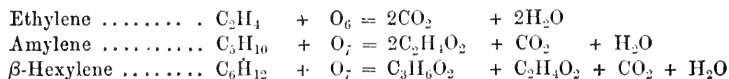
From fraction 1 we learn the presence of propionic acid, fraction 3 proves the presence of acetic acid, and fraction 2 proves that no other acids were present.

β -Hexylene, like amylene, was oxidized in a variety of ways, and always with the same result; we therefore conclude that it is decomposed by nascent oxygen, thus—

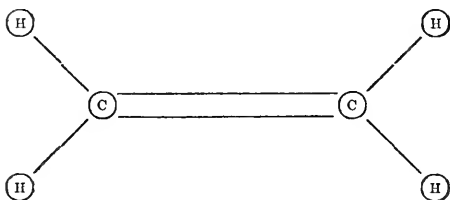
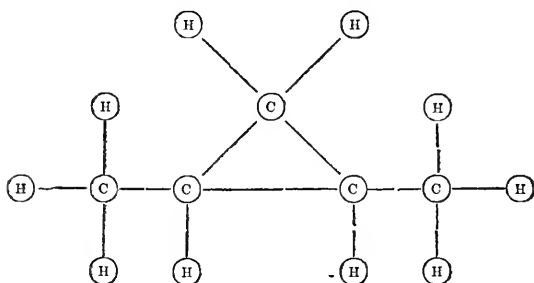
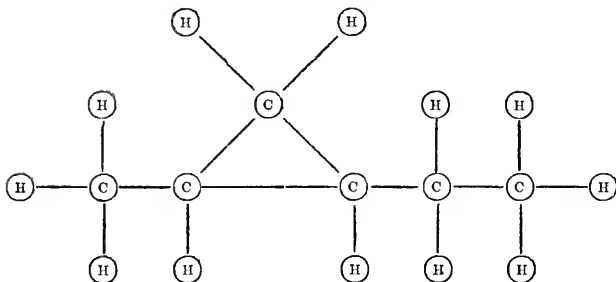


A few weeks prior to the publication of the above results, but unknown to us, M. Truchot published a paper on the oxidation of the olefines. His results differ remarkably from ours, but we believe we can explain the cause of the difference. M. Truchot states that amylene yields acids of the acetic series when oxidized with permanganate of potash, but that butyric, propionic, acetic, and formic acids are all formed. Now it is obvious that if this were really the case, gradual oxidation would be valueless as a method of research, for no possible information could be derived as to the molecular constitution of a body if molecules of every degree of complexity were formed by such oxidation. We have repeated the experiments of M. Truchot, and can to a certain extent verify his results; *i.e.*, if we oxidize amylene with *permanganate of potash*, we find that we can isolate acids, the salts of which contain a smaller proportion of base than corresponds to acetate. This, however, occurs only when the oxidizing agent is alkaline, and we find that even when it does occur, these higher acids may be made to split up by the action of oxidizing agents into acetic and carbonic acids. We conclude, therefore, that M. Truchot has insufficiently oxidized this olefine. It is, however, possible, and indeed probable, that he may have operated upon a mixture of isomeric olefines, in which case the complicated result obtained would be fully accounted for.

The following table shows the results of the oxidation of the olefines:—



These results induce us to propose the following graphic formulæ:—

Ethylene C_2H_4 .Amylene C_5H_{10} . β -Hexylene C_6H_{12} .

Whether these formulæ be correct or not is a question for the answering of which there are no data extant. There is, however, nothing inherently improbable in them, they represent the grouping indicated by the oxidation-products, and this consideration will, we trust, derive greater weight from the foregoing work.

We would draw attention to the relation subsisting between the oxidation-products of these two olefines and those of the secondary

alcohols obtained from them. The one, amylene, yields a secondary alcohol, the oxidation-products of which are, according to Wurtz,* identical with those of the olefine itself. He obtains, as the oxidation-products of amylene, acetone and acetic acid; that is to say, he obtains acetic acid and a substance which, by further oxidation, yields acetic and carbonic acids; and, moreover, he observes that it is somewhat difficult to obtain the acetone, thus confirming our statement. From the oxidation of the corresponding alcohol he obtained the same products, and, in addition, a small quantity of a substance having the composition of butylic alcohol. The method of its formation is not very clear. The assumption that oxidation has simply removed CH_2 , and left the substance from which this molecule has been subtracted still in the form of an alcohol, appears to us untenable. It seems to us possible that the substance in question may have been a mixture, perhaps of unaltered secondary amyl-alcohol and acetone. This view derives some probability from the fact that it is rather difficult completely to remove acetone from amyl-alcohol by the action of bisulphites. We have made such a mixture, and find that, even after 24 hours' standing, separation is not complete. We desire further to point out that this butyl-alcohol, if, as assumed by Dr. Debus, it be a secondary alcohol, would yield acids of a lower carbon condensation than itself to the action of oxidizing agents.

The alcohol obtained from β -hexylene does not yield the same oxidation-products as β -hexylene itself. This may possibly arise from the fact that the alcohol is not obtained from the olefine in the same manner as in the case of amylene. If this be the true reason, we should obtain a different alcohol by using oxide of silver to convert the iodide of β -hexyl into the alcohol.

In a former part of this paper we remarked that we had met with a sample of valerianic acid which did not resist the action of oxidizing agents. It split up and yielded carbonic and butyric acids. In a similar way there exists an amyl-alcohol which does not yield valerianic acid when oxidized; at least, so we infer from the following observations.

It has long been known that amyl-alcohol is not always found to boil at 132° . In fact, one variety of it boils at 128° . When we were searching for a pure sample of amyl-alcohol to be employed in the foregoing experiments, we received a sample from a distillery

* Ann. Ch. Pharm., Oct., 1864, p. 134.

in which rice was employed, though mixed with other grain, or, at any rate, spirit from other grain was mixed with rice-spirit before rectification.* After the fusel-oil had been put through all the ordinary purifying processes, such as washing, drying, digestion with potash, and repeated fractionation, it was found impossible to get it to boil at a constant temperature. In fact, it began to boil between 127° and 128° , the thermometer going up gradually and evenly to about 131° . With so small a difference between the boiling-points, it was obviously useless to attempt anything like a complete separation of the two liquids composing this mixture. Still, by repeated fractionation, especially as we had large quantities of the substance at command, we might accumulate a larger proportion of the substances of lower boiling-point in one fraction than existed in the original mixture. After many distillations a fraction was obtained which, though its boiling-point still rose to 131° towards the close of the distillation, passed over, for the most part, at a lower temperature. On the other hand, another fraction was obtained, the boiling-points of which were from 128° to 132° , the greater proportion of the liquid passing over near the latter. The former of these fractions we will designate fraction A, the latter fraction B. Two combustions were made of fraction A. Both yielded numbers corresponding to amyl-alcohol:—

	Substance taken	CO ₂	H ₂ O
I.	0.2248	0.5604	0.2742
II.	0.2646	0.6589	0.3176.

From these numbers we deduce the percentages:—

	I.	II.	Theory
C.....	67.97	67.91	68.18
H	13.55	13.33	13.63

The combustions were made with oxide of copper, chlorate of potash being employed at the close of the operation. Fraction A was then oxidized with chromic acid, in the manner so frequently before described, and the products of the operation fractionated. Carbonic acid was liberated during the oxidation.

* We state the above facts on the authority of the distiller, from whom we received this sample of fusel-oil.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·3748 0·4164	0·2800 0·3107	43·92 43·87	44·052	Butyric acid
Last fraction— 0·3768 0·4002	0·2583 0·2757	40·34 40·51	40·413	Valerianic acid

These acids are somewhat difficult to separate, requiring several repetitions of the fractionating process before the separation can be looked upon as complete. Carbonic, butyric, and valerianic acids appear, therefore, to be the products of the oxidation of this mixture. If the substance of lower boiling-point be really a secondary alcohol, yielding carbonic and butyric acids as its oxidation-products, we ought to have equivalent quantities of these substances produced. To determine this point, 1·2128 grm. of fraction A were introduced, in a sealed bulb, into the digestion-tube, which already contained bi-chromate of potash and sulphuric acid; the neck of the tube was drawn out to a long, fine point, and the digestion proceeded with. When it was judged that the digestion was complete, an india-rubber tube was slipped over the point and connected with a Liebig's potash-apparatus containing concentrated sulphuric acid. A second potash-apparatus, charged with potash, which had been weighed, was connected with the first. The point of the digestion-tube was then snipped off, and the carbonic acid escaping through the extremely small aperture, was dried by its passage through the sulphuric acid, and absorbed by the caustic potash. As soon as the passage of gas had completely ceased, the point of the digestion-tube was broken off somewhat lower down, though still within the india-rubber tube, and the contents heated until they boiled. The steam, of course, expelled the whole of the carbonic acid, and, by judiciously cooling the india-rubber tube and, when necessary, the top of the digestion-tube, any dangerously rapid absorption by the sulphuric acid was avoided. The potash-bulbs were then detached and reweighed. Of course their increase of weight gave a most accurate measure of the amount of carbonic acid liberated.

A precisely similar experiment was performed with fraction B.

As will be seen from the annexed numbers, the amount of carbonic acid differed considerably in the two cases :—

Substance employed.	Carbonic acid found.	Per cent. of carbonic acid.
Fraction A. 1·2128	0·4096	33·77
Fraction B. 1·5728	0·3636	23·09

Samples of each of the alcohols were oxidized as before, the contents of the digestion-tubes diluted and distilled almost to dryness, and samples of each acid distillate converted into baryta-salts. The annexed table exhibits the percentages of barium contained in these salts, and also those which would have been obtained on the assumption that an amount of butyric acid equivalent to the carbonic acid was produced, and that this butyric acid was the representative of the secondary alcohol contained in the two fractions. It is further assumed that the primary alcohol produced nothing but valerianic acid.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Calculated per centage.
Fraction A.			Fraction A.
0·4092	0·2975	42·75	42·801
0·3834	0·2784	42·69	
Fraction B.			Fraction B.
0·3192	0·2286	42·11	42·016
0·4206	0·3002	41·97	

Finally, a portion of the valerianic acid obtained by the oxidation of one of these samples of alcohol, was digested with dilute chromic acid (five per cent). No carbonic acid was liberated, thereby proving that the butyric and carbonic acids did not owe their existence to the decomposition of the valerianic acid.

We think that we have thus fairly proved the existence of a second isomeric, amyl-alcohol in the sample we were operating upon, though we were unable to isolate it.

We will now consider what information the method of research,

by gradual oxidation, is capable of affording us with regard to the molecular constitution of bodies. This question is best answered by considering how many isomers it is capable of revealing to us in any one case. Take for instance amyl-alcohol. We know that there are many possible isomers of this body, but gradual oxidation, or at least oxidation carried far enough to produce those substances which we have agreed to term proximate products of oxidation, could only reveal to us the existence of a portion of them; for it is obvious that we may have a pseudo-primary amyl-alcohol, *i.e.*, an alcohol containing a pseudo-amyl, say for instance propyl-ethyl; and we may have a secondary amyl-alcohol containing propyl and ethyl. Both these compounds would, we believe, yield the same proximate oxidation products, though doubtless the former would, in the first instance, yield pseudo-valerianic acid. This would at once distinguish it from the real primary alcohol, but would not distinguish it from the secondary alcohol, which would yield the same oxidation-products. Still, though the so-called proximate products of oxidation would not furnish us with information on this point, the *mediate* products taken in conjunction with the proximate products would.

We have not in the foregoing paper considered the case of bodies in which the ratio of carbon to hydrogen is such as to render it impossible to account for the whole of the carbon in the form of acids of the acetic series. It is obvious that such bodies must either yield substances of an altogether different class, or the carbon must be converted into carbonic acid.

XLV.—*On the Strength of Solutions of Phosphoric Acid of Various Densities.*

By Mr. JOHN WATTS, Senior Bell Scholar in the Laboratories of the Pharmaceutical Society.

[From the Proceedings of the British Pharmaceutical Conference, 1865, p. 39.]

IN the compilation of a table of this kind, the first thing is to know at what specific gravity to start; accordingly, finding that a thick syrupy acid of 1.5 p. c. sp. gr. contained nearly 50 per cent. PO_5 , I made that the starting-point, and proceeded regularly

downwards as far as sp. gr. 1·006. The interval between these two numbers contains 47 specific gravities, therefore 49 in all, and as the acid of each specific gravity was analysed at least three times, in order to obtain a correct mean, it entailed the work of about 150 analyses. The table, when completed, stands as follows:—

Specific Gravity.	Per-centage.	Specific Gravity.	Per-centage.	Specific Gravity.	Per-centage.	Specific Gravity.	Per-centage.	Specific Gravity.	Per-centage.
1·508	49·60	1·392	40·86	1·293	32·71	1·185	22·07	1·081	10·44*
1·492	48·41	1·384	40·12	1·285	31·94	1·173	20·91	1·073	9·53
1·476	47·10	1·376	39·66	1·276	31·03	1·162	19·73	1·066	8·62
1·464	45·63	1·369	39·21	1·268	30·13	1·153	18·81	1·056	7·39
1·453	45·38	1·256	38·00	1·257	29·16	1·144	17·89	1·047	6·17
1·442	44·13	1·247	37·37	1·247	28·24	1·136	16·95	1·031	4·15
1·434	43·25	1·239	36·74	1·236	27·30	1·124	15·64	1·022	3·03
1·426	43·28	1·228	36·15	1·226	26·36	1·113	14·33	1·014	1·91
1·418	42·61	1·215	34·82	1·211	24·79	1·109	13·25	1·006	·79
1·401	41·60	1·202	33·49	1·197	23·23	1·095	12·18		

I would next notice the method employed for its analysis. After assaying and testing the various advantages of a great many different processes, of which I will speak hereafter, I came to the conclusion that with a pure solution of phosphoric acid, no method is more simple, more accurate, or less liable to error, than the method employed in the British Pharmacopœia, viz., “the evaporation down of a weighed quantity of the solution, with a known excess of pure protoxide of lead.”

I confess I was somewhat disappointed when first employing this method, owing to the discordant results obtained, notwithstanding that at first sight it seemed exceedingly straightforward and plain; but I afterwards found it entirely arose from not operating with *pure* oxide. I had used the commercial article, and though previously to each analysis it had been carefully ignited, there nevertheless remained so much carbonate and other impurities, as to render it practically worthless, no two results agreeing nearer than 2 or 3 per cent.

Finding this to be the case, I looked about for some other substance to use instead, and for this purpose tried the oxide of zinc.

* British Pharmacopœia.

Analysis with this latter oxide gave perfectly accurate results as regards numbers, but was open to a great objection, inasmuch as the phosphate of zinc readily fuses; and upon ignition towards the end of the analysis to get rid of the last traces of water, the fusing of the phosphate, and its adhering tenaciously to the bottom of the crucible, from which it cannot be subsequently removed, entirely spoils the vessel for a second operation. Oxide of magnesia answered no better, for this, unlike the oxides of lead and zinc, forms a hydrate when put into water; and, as is the case with many magnesia salts, either the last traces of this water of hydration, or the atom of basic water assimilated when neutralizing the phosphoric acid, is so difficult to expel totally, even after powerful ignition, that one can never be certain that the whole of the water is driven off, unless the capsule has been allowed to cool and re-ignited several times, which, with such a number of similar analyses, causes much unnecessary trouble. The volumetric nitrate of uranium process was also tried, but as the results never approached nearer than 5 to 6 per cent., a discrepancy too great to be allowed in a case like this, it was given up. Determined then to revert again to oxide of lead, and to prepare a pure oxide myself, I took red lead ($2\text{PbO} \cdot \text{PbO}_2$), and dissolving out the protoxide with dilute nitric acid, washed well the resulting binoxide; this, by careful ignition over an air-flame, loses its extra oxygen-atom, and passes with incandescence to the state of protoxide. Working with oxide prepared in this manner, I obtained highly satisfactory results, and subsequently used this method only for the completion of the analyses in the table. By examining the gradation of the numbers on the table, it is seen that the percentage increases or decreases regularly accordingly as the specific gravity rises or falls, proving that the strength can be correctly deduced from a knowledge of its density, and that, unlike acetic acid, it presents no anomaly in this respect; also, that when a strong acid is diluted with water, though a considerable quantity of heat is evolved, no condensation in volume follows. The correctness of the numbers may be also somewhat checked in the following manner:—Take 100 *fluid* grains of 1.508 acid: this will weigh 150.8 grs., and contain 74.79 grs. by weight of PO_5 ; dilute this with 100 fl. grs. of water: the whole will weigh 250.8 grs., and contain 74.79 grs. by weight of PO_5 ; each 100 parts by weight will be therefore of sp. gr. 1.254, and contain theoretically 29.7 parts by weight of acid; by referring to the latter sp. gr. on

the table, we find by experiment such number to contain 29·16 per cent. Again, 100 fl. grs. of acid 1·285 sp. gr. will weigh 128·5 grs., and contain 41·03 grs. by weight of PO_5 ; diluted with 100 fl. grs. of water, it will weigh 228·5 grs., and contain 41·03 grs. of acid, being of sp. gr. 1·142; each 100 parts of acid of this sp. gr. should contain then 17·9 by weight of PO_5 . Reference to the table shows us 17·89 per cent. A great many numbers have been checked in this manner, and they were all found to be correct.

The temperature at which all the specific gravities were taken was 15·5 C. (60° Fahr.). This is, of course, an important point in using the table, as the volume of liquid varies considerably according to the temperature; and as at different heights of the thermometer comparison of volumes no longer holds good, comparison of percentages would be equally fallacious.

I may add that the acid used was prepared from common phosphorus in the ordinary manner; but I have since made several examples of acid from amorphous phosphorus, as first mentioned by Mr. Groves, and decidedly prefer this latter method; the phosphorus is readily acted upon, its use entails no danger, and a product is obtained in a few hours which ordinarily would take as many days. One little objection appeared, which is apt to make one think that the product is not absolutely pure, viz., that in the concentrated state it was more or less coloured, possessing a brownish or yellow tint; this might have arisen from the particular specimen of amorphous phosphorus operated on: probably another sample would not show this defect.

XLVI.—*Note on Messrs. Calvert and Johnson's paper "On the Action of Acids upon Metals and Alloys."*

(November, 1866, p. 434.)

By A. MATTHIESSEN, F.R.S.

IN most of the tables given in this paper (Tables 6—12) there will be found a column headed "Loss calculated according to the composition of the alloys." The numbers given under this heading are, however, all faulty, as the authors have calculated these

values from the weights of the metals composing the alloy, using the co-efficients, as they may be called, of the action of the acid on their surface as the co-efficients of the action of the acid on their weights; thus, in Table 7, p. 445, they give the following:—

Metals and composition of alloys.	Loss on 1 c.c.	Calculated loss on 1 sq. metre.	Loss calculated according to composition of alloy.
Copper	0·000	0·000	0·000
Zinc.....	0·200	333·33	333·33
1st alloy. Zn ₃ Cu			
Zn .. 83·70	0·155	258·334	279·00
Cu .. 16·30			
100·00			
Last alloy. ZnCu ₅			
Zn .. 17·05	0·000	0·000	56·83
Cu .. 82·95			
100·00			

Now 100 grms. of the first alloy consist of $\frac{83·7}{7·15} = 11·7$ c.c. zinc (for 1 c.c. weighs 7·15 grms.) and $\frac{16·3}{8·95} = 1·8$ c.c. of copper (for 1 c.c. copper weighs 8·95 grms.); or 1 c.c. of the alloy consists of 0·86 c.c. zinc and 0·14 c.c. copper.

The loss on 1 c.c. zinc by the action of hydrochloric acid being 0·200, on 0·86 c.c. it will be 0·172, and that of the acid on copper being 0·000, the calculated loss on 1 c.c. alloy is 0·172; or the calculated loss on the square meter, deduced from the composition of the alloy, will be 287, instead of 279, as given in the table.

Similarly the calculated loss on the alloy ZnCu₅ will be 68 instead of 56·83.

The authors' method of calculation is, as stated, the use of weight instead of surface; thus their calculated values are found by multiplying the weight-percentages by the co-efficients, and dividing by 100; for $83·7 \times 3·3333 = 279$; and

$$17·05 \times 3·3333 = 56·83.$$

The whole of these results, therefore, need recalculation.

It would have been of interest had the authors stated how they made the copper-zinc alloys in exactly their combining proportions, as they must have had great difficulty in doing so, owing to the volatility of zinc.

XLVII.—*On the Isomorphism of Thallium-Perchlorate with the Potassium and Ammonium-Perchlorates.*

By Prof. H. E. Roscoe, F.R.S., &c.

[From the Proceedings of the Literary and Philosophical Society at Manchester
October 16, 1866.]

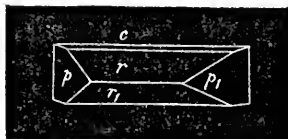
THE recently ascertained isomorphism of the thallium- and ammonium-sulphates* renders it highly probable that the perchlorates of these metals also exhibit isomorphous relations.

Thallium-perchlorate equals the alkaline-perchlorates in stability. It can be readily prepared either by dissolving metallic thallium in aqueous perchloric acid, or by the double decomposition of thallium-sulphate and barium-perchlorate. From solution the anhydrous salt is easily deposited in colourless rhombic crystals, which are transparent, bright, well-defined, and non-deliquescent. The specific gravity of the crystals is 4·844 at 15°·5 C.; they dissolve in 10 times their weight of water at 15°, and in about $\frac{3}{8}$ ths of their weight of water at 100°; the salt is also slightly soluble in alcohol. Thallium-perchlorate does not lose weight when heated to 200° C., and the temperature may even be raised to within a few degrees of the boiling point of mercury without producing the slightest decomposition of the salt. On the further application of heat a black mass is formed, and the salt finally volatilises as thallium-chloride.

The crystalline form of thallium-perchlorate is that of a right rhombic prism (pp_1), in which the faces of the rhombic octohedron (rr_1) and the basal faces of the prism (c) generally appear, the crystals being lengthened, as is the case with the alkaline-perchlorates sometimes in the direction of the prismatic, and sometimes in the direction of the octohedral faces. A careful measurement

* Lang, Phil. Mag. xxv, 248.

of the crystals gave the mean value of $102^\circ 50'$ for the angle pp_1 ; and that of $102^\circ 6'$ for the angle rr_1 on c . Hence the relation of the axes is $0.7978 : 1 : 0.6449$.



The angles observed by Mitscherlich (Pogg. Ann. xxv., 301), in the case of potassium and ammonium-perchlorates agree exactly with the above; for the first of these salts, $pp_1 = 103^\circ 58'$, rr_1 on $c = 101^\circ 19'$; and for the second, $pp_1 = 103^\circ 11'$, and rr_1 on $c = 102^\circ 4'$, giving the relation of the axes to be (1) $0.7817 : 1 : 0.6408$ and (2) $0.7926 : 1 : 0.6410$. An analysis, made in my laboratory by Mr. T. E. Thorpe, shows that the formula of the salt is Ti Cl O_4 .

(1.) *Determination of Thallium.*—The crystals were well dried in vacuo over sulphuric acid, and precipitated with platinum-tetrachloride, the passage of the finely divided precipitate through the filter being avoided by evaporating to dryness on the water-bath, and taking up with absolute alcohol. (a) Salt prepared by direct solution of the metal in perchloric acid; 0.1831 salt yielded 0.2476 chloroplatinate. (b) Salt prepared by double decomposition; 0.4502 salt yielded 0.6060 chloroplatinate.

(2.) *Determination of Perchloric Acid.*—A solution of potassium-acetate was added to the thallium-perchlorate, and the whole evaporated to dryness on a water-bath, the acetates of thallium and potassium washed out with absolute alcohol, and the insoluble potassium-perchlorate collected on a weighed filter; 0.4570 thallium-perchlorate yielded 0.2100 potassium-perchlorate. Hence :

		Calculated.		Found.	
			I.	II.	III.
Tl.	204.0	67.21	67.38 (a)	67.18 (b)	} 32.96
Cl.	35.5	21.09			
O ₄	64.0	11.70			
	<hr/>	<hr/>			
	303.5	100.00			

P R O C E E D I N G S

AT THE

MEETINGS OF THE CHEMICAL SOCIETY, 1866.

January 18th.

Dr. Miller, F.R.S., President, in the Chair.

Robert Henry Smith, Rodney-street, Pentonville; James Spier, Newcastle-on-Tyne; Thomas Boverton Redwood, 19, Montague-street, Russell-square; John Conroy, Oxford; were elected Fellows; and John Jones, Newport, Monmouthshire, was re-admitted a Fellow.

The following papers were read :—

“On Pyrophosphotriamic Acid :” by Dr. Gladstone.

“On the Action of Carbonic Oxide upon Sodium-ethyl :” by Prof. Wanklyn.

“On Glyoxylic Acid :” by Dr. Debus.

February 1st.

Dr. Miller, F.R.S., President, in the Chair.

Franklin Epps, 112, Great Russell-street; William Thorp, 13, York-terrace, Kingsland-road; Edward Purser, Jun., 116, Fenchurch-street; Arthur Ellson Davies, Surgeons' Hall, Edinburgh; were elected Fellows.

Dr. Gilbert delivered a discourse “On the Composition, Value, and Utilisation of Town Sewage.”

February 15th.

Dr. Frankland, F.R.S., Foreign Secretary, in the Chair.

G. B. Ferguson, Magdalen Hall, Oxford; W. H. Walenn, 19, Talbot-road, Tufnell Park West; Benjamin Nichols, Making-place Hall, Rippenden, near Halifax; were elected Fellows. Twelve Fellows were removed from the Society for non-payment of their subscriptions.

The following papers were read:—

“On the Action of Nitrous Acid upon Naphthylamine:” by Ernest T. Chapman, Esq.

“On the Action of Heat on Ferric Hydrate in presence of Water:” by Edward Davies, Esq.

“On the Prognosis of New Alcohols and Aldehydes:” by Prof. Kolbe.

March 1st.

Dr. Williamson, Vice-President, in the Chair.

Robert Bell, Queen's College, Kingston, Canada West; W. H. Corfield, Pembroke College, Oxford; G. W. Webster, Bridge-street, Warrington; were elected Fellows.

The following papers were read:—

“On New and Rare Cornish Minerals:” by Prof. Church.

“On the Numerical Relations between the Atomic Weights of the Elements:” by J. A. R. Newlands, Esq.

“On a New Method of forming Organo-metallic bodies:” by Prof. Wanklyn.

“On the Chemical Action of Sunlight upon Sensitive Photographic Papers:” by C. R. Wright, B.Sc.

March 15th.

Dr. Miller, F.R.S., President, in the Chair.

Samuel Crawley, Training College, York; Charles Patmore Phillips, 109, Fenchurch-street; were elected Fellows.

The following paper was read :—

“On Hydrocyan-rosaniline:” by Dr. Hugo Müller.

Dr. Frankland gave a verbal account of some “Variations in the Composition of the Waters supplied to the Metropolis during the past year.”

March 29th.

Anniversary Meeting.

Dr. Miller, F.R.S., President, in the Chair.

The following report was read by the President :—

On this 25th anniversary of the establishment of the Chemical Society, the Council are again able to congratulate the Fellows upon a steady advance in their numbers, and a prosperous condition of their finances.

On the last anniversary the numbers enrolled as Fellows amounted to 453, whilst on the present occasion 482 appear upon our list.

These numbers are accounted for as follows :—

Number of Fellows at last anniversary (1865)	453
Elected and paid since	47
	<hr/>
	500
Removed on account of arrears.	12
Fellows withdrawn	3
„ deceased.	3
	<hr/>
	— 18
	<hr/>
Present number of Fellows (1866)	482
	<hr/>
Number of Foreign Members last Anniversary	38
Deceased	1
	<hr/>
Present number	37

The names of the Fellows withdrawn are:—J. E. Davidson, Wm. Wakefield, Samuel Parr.

The names of the Fellows deceased are:—Prof. W. T. Brande, Dr. Daughlish, Mr. George Smith, of the firm of Messrs. Smith and Co., distillers; Professor Rafaele Piria.

The name of Mr. Brande has been for more than fifty years familiar to the public, as one of the most prominent chemists of this country. Contemporary, in his prime, with Davy, Dalton and Wollaston, he was one of the few survivors of a generation who formed the connecting link between the great chemists of the last century, Watt, Priestley, and Cavendish, and those who are engaged in carrying forward their work at the present time.

Wm. Thomas Brande, D.C.L., F.R.S., was descended from a family of Hanoverian extraction, and was the younger son of Mr. Brande, the apothecary to George III. and Queen Charlotte. He was born in 1786, and educated at Westminster School. As a boy he attracted the notice of Mr. Hatchett, of the Mint, from whom he appears to have derived his first taste for chemistry. When he left school, he went for a time to Hanover, and on his return to England entered as a medical student at St. George's Hospital, where in 1805 and 1806 he attended the chemical lectures of Dr. Pearson and Mr. Accum. In 1808 he made a chemical examination of the calculi in the Hunterian Museum, and in the same year commenced his career as a public lecturer by delivering a course on Pharmaceutical Chemistry in Dr. Hooper's Medical School, in Cork Street. Shortly afterwards he joined the Medical School in Windmill Street, where for several years he lectured on general chemistry. In 1813, on the recommendation of Sir H. Davy, he was appointed as his successor in the chair of chemistry in the Royal Institution. The chemical classes of St. George's Hospital and of the Windmill Street School were afterwards transferred to the Royal Institution, so that in addition to his ordinary duties as Professor, he gave an extended course of chemical lectures in the laboratory of the Institution. In this course Mr. Faraday was associated with him in the year 1827, and for nearly twenty years they lectured together. He continued to hold his professorship until the year 1852, when he resigned his active duties, and was appointed Honorary Professor to the Royal Institution. As a lecturer, Mr. Brande was highly successful, being distinguished for the clearness of his

style, for the methodical arrangement of his matter, as well as for the admirable selection and performance of his experimental illustrations.

In 1809, he was elected a Fellow of the Royal Society, and in 1816 succeeded Dr. Wollaston as one of its secretaries, in which capacity he acted until the year 1824. He received the Copley Medal of the Society in 1813, for his researches on the proportion of alcohol in wines, and for his experiments on some of the compounds of carbon and hydrogen; and in 1828 he received the Fullerman Medal of the Royal Institution.

Having in 1812 been requested to report upon the laboratories belonging to the Society of Apothecaries in London, he was shortly afterwards appointed Professor of Chemistry and Materia Medica to that corporation, and in 1851 filled the Chair of Master of the Company.

We learn from the autobiography of the late Sir B. Brodie, that about the year 1812, Mr. Brande became a member of a small scientific society, the Animal Chemistry Club, which included Sir E. Home, Sir H. Davy, Sir B. Brodie himself, Mr. Hatchett, Dr. Babington, Mr. Children, and some other distinguished chemists and physiologists. It was chiefly a social gathering intended especially to stimulate researches upon physiological chemistry.

In the year 1818, Mr. Brande married Mr. Hatchett's youngest daughter, and this lady has survived him. In 1825 he received the appointment of Keeper of the Dies at the Mint, and on the change in the management of the Mint in 1852, he was appointed Superintendent of the Coining department.

As a scientific writer Mr. Brande is well known. The first edition of his *Manual of Chemistry* appeared in 1815. It passed through six editions, the last of which was published in 1848. Since that time it has not been republished; but in connection with Dr. Taylor, in 1863, a joint work on chemistry, based largely upon Mr. Brande's manual, appeared. For sixteen years, from 1816 to 1832, he, conjointly with Mr. Faraday, edited the "*Quarterly Journal of Science and Art*." He was also the author of a "*Dictionary of Pharmacy*," as well as of a work entitled "*Outlines of Geology*," besides acting as editor of a "*Dictionary of Science, Literature, and Art*," upon the second edition of which he was occupied at the time of his death.

In 1836, Mr. Brande was named one of the original Fellows

of the University of London, and a member of its Senate; in 1846 he became one of their Examiners in Chemistry, in which capacity he continued to act until the year 1858. On the installation of Lord Derby as Chancellor of the University of Oxford, Mr. Brande received the honorary degree of D.C.L. in that University. He was also a Fellow of various scientific societies, both in this country and abroad.

His name will always be connected with the early history of the Chemical Society. On the establishment of the Society in 1841, Mr. Graham became its first President, and Mr. Brande and Professor Daniell, with Mr. J. T. Cooper and Mr. R. Phillips, were nominated Vice-Presidents. In March, 1847, Mr. Brande was elected to the office of President, and as it was in this year that the Society obtained its charter of incorporation, his name appears as its President in the deed of incorporation.

It was during Mr. Brande's Presidency that the Society began the publication of a Quarterly Journal, to which he contributed a short paper on the Well-water of the Mint.

To the last he preserved his vigour both of body and mind, so that even, at the advanced age of 81, the news of his death after a short illness, was received almost with a feeling of surprise.

Dr. John Daughlish was born in the year 1824, in the parish of Bethnal-green, London. He was educated at the school of Dr. Alexander Allen, at Hackney, and began the study of medicine in 1852 at the University of Edinburgh, where he subsequently took his degree of M.D. He was elected a Fellow of the Chemical Society, June 20th, 1861. He has not communicated any paper to its Transactions, but is well known in connection with a patented process for making unfermented bread, which bears his name, and which has come extensively into use.

In this process, carbonic anhydride is liberated from chalk by the action of sulphuric acid, the gas is received into an ordinary gasholder, and is thence pumped into a strong cylindrical vessel containing water, by which means a solution of carbonic acid containing three or four times its bulk of the gas is obtained. The solution of carbonic acid is drawn off into a strong closed vessel, where it is mixed under pressure by means of a revolving agitator, with the proper proportion of flour and salt. When the incorporation has been properly effected, a valve at the bottom of the

mixing vessel is opened, the dough escapes, and on coming into the outer atmosphere immediately becomes vesicular, owing to the expansion of the imprisoned gaseous carbonic anhydride, as soon as it is released from the pressure to which it has been subjected. It is immediately transferred to the oven and baked.

This process is a substantial addition to the supply of bread in the country; for besides ensuring cleanliness by dispensing with the ordinary method of kneading by the naked hands or feet, it saves a sensible percentage of the flour, which was wasted in the old process of fermentation. It also dispenses with the necessity of the use of alum, formerly resorted to for preventing the conversion of starch into glucose, which is so liable to occur in flour from the more highly azotised wheats; and it is even more digestible than the bread fermented upon the ordinary plan.

Dr. Daughlish died on the 14th of January, 1866, at the early age of 42. Those who knew him have to regret the loss of an able and accomplished man, and the Society that of an energetic, practical worker.

Rafaele Piria was born at Scilla, in Calabria, on the second of August, 1815. In 1838 he was a pupil of M. Dumas, in whose laboratory he made his classical research on Salicin and its derivatives. This laborious investigation, surrounded as it was with many and formidable difficulties, he carried out with the most persevering industry, establishing the proximate constituents of salicin to be grape-sugar and saligenin. The latter substance he transformed by dilute acids into saliretin, by concentrated sulphuric acid into rutilin, by cold nitric acid into helicin, and by more powerful oxidizing agents into formic acid and hydride of salicyl. The latter substance was soon recognised as the essential oil of meadow-sweet, the constitution of which was thus for the first time clearly established. This splendid investigation, to which we owe almost exclusively our very complete knowledge of the salicyl series of organic bodies, is justly regarded as a model of analytical accuracy and logical reasoning.

M. Piria was not content with the reputation which this great work secured for him, but continued down to a recent period to contribute numerous memoirs to chemical literature. Amongst the most important of these, his papers on Asparagin, Populin, and Nitrosalicylic Acid may be mentioned. His last memoir, however,

is perhaps in its general bearing upon organic chemistry, the most important of all. It appeared in 1856, and described a method of general application for the conversion of organic acids into the corresponding aldehydes, by distilling their calcium-salts with calcic formiate. The true significance of this reaction is at once perceived when it is remembered that it furnished the first step in the passage from the *acid* into the *alcohol* family, the second having been since supplied by Wurtz in the transformation of the aldehydes into their corresponding alcohols by nascent hydrogen. Soon after the contribution of this valuable discovery, M. Piria's energies became absorbed in a movement which could not fail to attract the services of Italy's best intellects. He became a senator in the Parliament of the new kingdom; nevertheless he did not allow himself to be entirely withdrawn from science, but continued to hold his professorship at the University of Turin until his death, which took place at Turin, on the 18th of July, 1865.

List of Papers read at the meetings of the Chemical Society from March 30, 1864, to March 30, 1865:—

1. "On a New Bromine-derivative of Camphor:" by Mr. W. H. Perkin.
2. "On a Deposit of Sulphate of Ammonia from Dried Blood:" by Mr. J. A. R. Newlands.
3. "Laboratory Notices:" by Prof. Bloxam.
4. "On Phosphide of Magnesium:" by Mr. J. P. Blunt.
5. "On the Periodides of some Organic Bases:" by Mr. W. A. Tilden.
6. "On the Specific Refractive Energies of Elements and their Compounds:" by Dr. Gladstone.
7. "On the Transformation of the Lactic into the Acrylic Series of Acids:" by Messrs. Frankland and Duppa.
8. "On the Action of Nascent Hydrogen on Azodinaphthyl-diamine:" by Mr. W. H. Perkin.
9. "On Some New Cornish Minerals:" by Prof. Church.
10. "On the Caprylic and CEnanthylic Alcohols:" by Mr. E. Chapman.
11. "On the Absorption of Gases by Charcoal:" by Mr. John Hunter.
12. "On Nitro-Compounds:" by Dr. S. J. Mills.
13. "On Pyrophospho-diamic Acid:" by Dr. Gladstone.

14. "On Phenyl-Phosphoric Acid:" by Dr. H. Müller.
15. "On the Material to be Employed for Mural Standards of Length:" by Mr. James Yates.
16. "On Pyrophospho-triamic Acid:" by Dr. Gladstone.
17. "On the Action of Carbonic Oxide on Sodium-ethyl:" by Prof. Wanklyn.
18. "On the Constitution of Glyoxylic Acid:" by Dr. Debus.
19. "On the Action of Nitrous Acid upon Naphthylamine:" by Mr. E. Chapman.
20. "On the Action of Heat on Ferric Hydrate in presence of Water:" by Mr. E. Davies.
21. "On the Prognosis of New Alcohols and Aldehydes:" by Prof. Kolbe.
22. "Further Researches on New Cornish Minerals:" by Prof. Church.
23. "On the Numerical Relations of the Atomic Weights of the Elements:" by Mr. J. A. R. Newlands.
24. "On a New Mode of forming Organo-Metallic Bodies:" by Prof. Wanklyn.
25. "On the Chemical Action of Sunlight upon Sensitive Photographic Papers:" by Mr. C. R. Wright.
26. "On Hydrocyan-Rosaniline:" by Dr. H. Müller.

Lectures have also been given.

1. "On Some Points in the Analysis of Potable Waters:" by Dr. Miller, President.
2. "On the Composition, Value, and Utilisation of Town Sewage:" by Messrs. Lawes and Gilbert.

The following Fellows were elected Officers and Council for the ensuing year:—

President.—W. A. Miller, M.D., F.R.S.

Vice-Presidents who have filled the Office of President.—Sir B. C. Brodie, F.R.S.; C. G. B. Daubeny, M.D., F.R.S.; Thomas Graham, F.R.S.; A. W. Hofmann, LL.D., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, Ph.D., F.R.S.; Colonel Philip Yorke, F.R.S.

Vice-Presidents.—F. A. Abel, F.R.S.; Walter Crum, F.R.S.; Warren De la Rue, Ph.D., F.R.S.; John Stenhouse, LL.D., F.R.S.

Secretaries.—William Odling, M.B., F.R.S.; A. V. Harcourt, M.A.

Foreign Secretary.—E. Frankland, Ph.D., F.R.S.

Treasurer.—Theophilus Redwood, Ph.D.

Other Members of the Council.—F. Grace Calvert, F.R.S.; Dugald Campbell, W. Crookes, F.R.S.; H. Debus, Ph.D., F.R.S.; F. Field, F.R.S.; G. C. Foster; E. A. Hadow; H. Lethaby, Ph.D.; Hugo Müller, Ph.D.; H. M. Noad, Ph.D., F.R.S.; W. J. Russell, Ph.D.; Maxwell Simpson, Ph.D., F.R.S.

It was resolved that the fourth Bye-law, relating to the removal of Fellows, be altered as recommended by a resolution of Council, passed at a meeting held on January 18th.

It was resolved that a new form of Nomination paper for the proposal of Gentlemen as Fellows of the Society, as approved by the Council, should be adopted.

The thanks of the Society were voted to the President, Officers, Council, and Auditors, for their services during the past year.

The Treasurer presented the Balance-sheet of the Society.

THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY.

CRS.

1865-6. March 25.	1865-6. Journal.	£ s. d.	£ s. d.	£ s. d.
To Balance on hand, 25th March, 1865	1865-6. Journal.	792 8 11	By Editor's Salary	95 0 0
" Dividends on £1,300 Consols		38 7 0	" Printing Journal	168 17 0
" Sundry Receipts from 25th March, 1865, to 27th March, 1866:—			" Engraving for ditto	15 4 0
Admission Fees			" Distributing ditto	44 1 5
Life Compositions			" Reporting Proceedings	17 17 0
27 Subscriptions for 1864 and previous years			" Translation	0 12 0
83 Subscriptions for 1865			" Annual Subscription for Proceedings sent to the Fellows of the Chemical Society	50 0 0
280 Subscriptions for 1866			Librarian's Salary	25 0 0
Subscriptions overpaid carried to account			" Books and Magazines	3 16 0
			" Bookbinding	7 9 7
			Collector's Commission	42 10 0
			" Clerk	3 0 0
			Printing Notices	1 10 0
			" Stationery	2 0 0
			" Stamps	1 2 4
			Royal Society, Share of Tea Expenses	15 11 8
			" T. J. Hux, Salary	20 0 0
			" Petty Expenses per Book	3 4 0
			" " Gas Account	2 8 0
			" W. Page, Cleaning	1 0 0
			" Gate Porter	2 2 0
			Ventilating Meeting Room, and Altering book-cases	
			Purchase of £300 3 per Cent. Consols	123 2 0
			" Balance at Messrs Coutts	273 7 6
				762 8 11
				£ 1681 0 5

ASSETS.

Balance at Coutts's

Invested in Three per Cent. Consols

£ 2,062 8 11

We have examined the accounts of the Chemical Society from the 25th March, 1865, to the 23rd March, 1866, inclusive, compared them with the vouchers, and found them correct. We find the balance in favour of the Society to be £762 8s. 11d., which is at the Society's bankers.

JOHN ATTFIELD, }
CHAS. HEISCH, } *Editors.*

London, March 27th, 1866.

April 5th.

Dr. Hofmann, F.R.S., Vice-President, in the Chair.

Robert McCalmont, Belfast; Wm. Carr Stevens, Mark Lane; Thomas Vosper Nightingale, Manchester, were elected Fellows.

The following papers were read:—

“On the Estimation of Phosphorus in Iron and Steel:” by J. Spiller, Esq.

“On Magnesium:” by Prof. Wanklyn and E. T. Chapman, Esq.

“Note on Mercury-ethyl:” by E. T. Chapman, Esq.

“Contributions to the History of the Periodides of the Organic Bases:” by W. A. Tilden, Esq.

“On the Formation of Acetylene:” by H. McLeod, Esq.

“On the Synthesis of Guanidine:” by Dr. Hofmann.

April 19th.

Dr. Miller, President, in the Chair.

J. T. Brown, Oxford Villa, Sudbury; James Gale, Belsize Park, Hampstead; Wm. Huggon, Park Row, Leeds; Joseph Richardson, Dawson-street, Manchester; Wm. Marshall Watts, B. Sc., University Laboratory, Glasgow, were elected Fellows.

The following papers were read:—

“On Picric Ether:” by Dr. Stenhouse and Dr. H. Müller.

“On Styplmic Ether:” by Dr. Stenhouse.

Professor Cary Foster delivered a discourse “On the Thermal Phenomena accompanying Chemical Action.”

May 3rd.

Dr. Miller, F.R.S., President, in the Chair.

Marshall Hall, Cleveland-terrace, Hyde Park; John Robinson, Oxford; J. J. Lundy, Leith; were elected Fellows.

Professors Rammelsberg, Wolcott Gibbs, and Weltzien, were elected Foreign Members.

The following papers were read :—

“On Pyrophosphodiamic Acid :” by Dr. Gladstone.

“On the Phosphates of Calcium, and the Solubility of Tricalcic Phosphate :” by R. Warrington, Jun., Esq.

May 17th.

Dr. Miller, F.R.S., President, in the Chair.

The following papers were read :—

“On the Production of Acetic and Propionic Acids from Amylic Alcohol :” by E. T. Chapman, Esq.

“On the Oxidation of Ethylamine :” by Prof. Wanklyn and E. T. Chapman, Esq.

“On the Action of Acids on Naphthylamine :” by E. T. Chapman, Esq.

“On some Compounds obtained from Acetone :” by Sir Robert Kane.

“On Formulæ for the Expansion of Gases by Heat :” by the Rev. B. W. Gibbons.

“On the Nitro-prussides :” by E. A. Hadow, Esq.

June 7th.

Dr. Miller, F.R.S., President, in the Chair.

Wm. Arnot, Bachelor-street, Liverpool; E. H. Davies, Harley-road, Brompton; C. Wilson, Bridgewater Smelting Company, St. Helen's; C. R. A. Wright, B. Sc.; were elected Fellows.

The following papers were read :—

“On the Oxidation-products of the Propione produced from Carbonic Oxide and Sodium-ethyl :” by Prof. Wanklyn.

“On Phthalic Aldehyde :” by Prof. Kolbe and G. Wirthin.

“On Chrysammic Acid :” by Dr. Stenhouse and Dr. H. Müller.

“On Chrysammic Ether :” by Dr. Stenhouse.

"On the Platinum-bases:" by E. A. Hadow, Esq.

"On Decompositions of Nitrite of Amyl:" by E. T. Chapman, Esq.

"On a Cyanogen-derivative of Marsh-Gas:" by Henry Bassett, Esq.

Mr. A. Vernon Harcourt delivered a lecture "On the Observation of the course of Chemical Change."

June 21st.

Dr. Williamson, Vice-President, in the Chair.

Arthur Gamgee, M.D., Edinburgh; James H. Lighbown, Manchester; W. F. K. Stock, Darlington, Durham; Edward J. Sparks, Oxford; were elected Fellows.

The following papers were read:—

"On the Action of Acids upon Metals and Alloys:" by Prof. Crace Calvert and R. Johnson, Esq.

Dr. Debus delivered a lecture "On the Constitution of some Carbon-compounds."

July 5th.

Extra Meeting.

Dr. Miller, F.R.S., President, in the Chair.

Mr. James Yates exhibited and described some new Mural Standards of Length made in Porcelain by Mr. Casella.

The following papers were read:—

"On the Constitution and Representation of Organic Compounds:" by Dr. Williamson.

"On the Reduction of the Oxides of Nitrogen by Metallic Copper in Organic Analysis:" by W. Thorp, Esq.

"On the Hydrocarbons contained in Crude Benzol:" by C. Schorlemmer, Ph.D.

"On Ethyl-hexyl Ether:" by C. Schorlemmer, Ph.D.

November 1st, 1866.

Dr. Miller, F.R.S., President, in the Chair.

W. Chandler Roberts, Camberwell New Road, Kennington Park; E. P. H. Vaughan, Gaisford-street, Kentish Town, were elected Fellows.

The following papers were read:—

“On an Instrument for Taking the Specific Gravities of Heterogeneous Liquids:” by Dr. H. Sprengel.

“On the Relation between the Products of Gradual Oxidation, and the Molecular Constitution of the bodies Oxidised:” by E. T. Chapman, Esq., and W. Thorp, Esq.

November 15th.

Dr. Miller, F.R.S., President, in the Chair.

W. H. Gossage, Melbourne, Victoria; R. Biggs, Charles-street, Bath; David Page, Galibech Powder Mills, Kendal, were elected Fellows.

The following papers were read:—

“On Atmospheric Ozone;” by Dr. Daubeny.

“On a Chlorosulphide of Carbon:” by W. N. Hartley, Esq.

“On the relation between the Products of Gradual Oxidation, and the Molecular Constitution of the bodies Oxidised:” Part II., by E. T. Chapman, Esq., and W. Thorp, Esq.

“On the Synthesis of Butylene:” by E. T. Chapman, Esq.

December 6th.

Dr. Miller, F.R.S., President, in the Chair.

A. C. Cook, Ph.D. King's College, London; Henry Dircks, C.E., Bucklersbury; James Forrest, Ashburnam Road, Greenwich; Wm. Hutchinson, Gray's Inn Road; A. F. Marreco, Newcastle College of Medicine; J. Hancock Richardson, Newcastle-on-Tyne, were elected Fellows.

The following papers were read :—

“On the Synthesis of Formic Acid :” by E. T. Chapman, Esq.

“On the Alloys of Magnesium :” by Jas. Parkinson, Esq.

“On the Oxidation of Ethylic Benzoate :” by R. H. Smith, Esq.

December 20th.

Dugald Campbell, Esq., in the Chair.

John Broughton, Esq., Government Cinchona Plantation, Madras Presidency; Watson Smith, Portland Crescent, Manchester; Walter Noel Hartley, Esq., Pathological Laboratory, St. Thomas's Hospital; Alex. Morrison Thomson, D.Sc., University of Sydney, New South Wales, were elected Fellows.

The following papers were read :—

“On the Basicity of Tartaric Acid :” by W. H. Perkin, Esq.

“On the Absorption of Vapours by Charcoal :” by J. Hunter, M.A.

“On Some Reactions of Hydriodic Acid :” by E. T. Chapman, Esq.

“On a New Continuous Aspirator :” by H. McLeod, Esq.

Donations to the Library in the year 1866 :—

“A Dictionary of Chemistry and the Allied Branches of other Sciences :” by Henry Watts. Parts XXXIII.—XXXVI. :

from Messrs. Longman and Co.

“Lectures on Animal Chemistry delivered at the Royal College of Physicians :” by William Odling, M.B. : from the Author.

“Elements of Chemistry, Theoretical and Practical,” 3rd Edition, Part III. : by William Allen Miller, M.D., LL.D. :

from the Author.

“Lecture Notes for Chemical Students, embracing Mineral and Organic Chemistry :” by E. Frankland, Ph.D., F.R.S. :

from the Author.

“Lessons on Elementary Chemistry :” by Henry E. Roscoe, B.A., F.R.S. :

from the Author.

“Chemical Handicraft :” by J. J. Griffin : from the Author.

“Synoptic Tables of Chemistry :” by A. F. Foureroy :

from George Whipple, Esq.

“The Chemical Laboratories of the Universities of Bonn and Berlin :” by A. W. Hofmann, Ph.D., F.R.S. : from the Author.

“Chemical Addenda, being a brief exposition of the salient features of Modern Chemistry :” by the Rev. B. W. Gibsons :

from the Author.

“Little Experiments for Little Chemists :” by M. H. Walenn :

from the Author.

“The Toxicologist’s Guide :” by J. C. Horsley :

from the Author.

“Mineral Resources of Central Italy, including a description of the Mines and Marble Quarries :” by W. P. Jervis :

from the Author.

“On the Application of Disinfectants in arresting the Spread of the Cattle Plague :” by William Crookes, F.R.S. :

from the Author.

“The Book of Quinte Essence, or the Fifth Being; that is to say, Man’s Heaven :” edited from the Sloane MS. 73, about 1460–70 A.D. : by Federick J. Furnivall, M.A., and published by the Early English Text Society :

from the Editor.

“Report on Experiments undertaken by order of the Board of Trade, to determine the Relative Values of Unmalted and Malted Barley as Food for Stock :” by J. B. Lawes, Esq. :

from the Author.

“First Report of the Commissioners appointed to inquire into the best means of preventing the Pollution of Rivers (River Thames) :” Vol. I., Report, Appendix, and Plans; Vol. II. Minutes of Evidence and Index :

from the Commissioners.

“Abridgements of Specifications of Patents relating to Electricity and Magnetism :” compiled by Mr. H. Walmers :

from the Compiler.

“Address on the Presentation of the Gold Medal of the Royal Astronomical Society to John Couch Adams, Esq., M.A. :” by the President, Warren De La Rue, Ph.D., F.R.S. :

from the Author.

“On the Source of Muscular Power :” by E. Frankland, Ph.D., F.R.S. :

from the Author.

“Synthetical Researches on the Ethers, No. 1; Synthesis of Ethers from Acetic Ether :” by E. Frankland and B. F. Duppá :

from the Authors.

"Lord Bacon as Natural Philosopher; a reply to an article by Baron Liebig, bearing the same title:" by G. F. Rodwell:

from the Author.

"Suggestions for a new System of Chemical Nomenclature:" by George Hamilton:

from the Author.

"Analyses of the Waters of Pyrmont and Driburg:" by R. Fresenius:

from the Author.

Pamphlets: by Dr. A. Völeker:

from the Author.

"On the Absorption of Potash."

"On the Functions of Soda-salts in Agriculture."

"On the Absorption of Soluble Phosphate of Lime by different Soils of known Composition."

"On Peruvian Guano."

"Salt Experiments and Mangolds."

"On Disinfectants."

"On the Composition of Orange Globe Mangolds: Bulbs and Tops."

"Annual Report of Chemical Analyses:"

Pamphlets: by C. M. Wetherill:

from the Author.

"On the Crystalline Nature of Glass."

"Experiments with Ammonium-amalgam."

"On the Crystallisation of Sulphur, and upon the Reaction between Sulphide of Hydrogen, Ammonia, and Alcohol."

"A brief Sketch of the Modern Theory of Chemical Types:"

"Cours de Philosophie Chimique; fait au Collège de France:" par Adolphe Wurtz (1864—1866):

from the Author.

"Sur l'Isomérisme:" par M. Berthelot:

from the Author.

"Nouvelles Recherches sur les Lois des Proportions Chimiques, sur les Poids Atomiques, et leur Rapports Mutuels:" par J. S. Stas:

from the Author.

"Sur le Dosage de l'Acide Tartrique:" par M. Berthelot:

from the Author.

"Sur les Oxydes du Niobium:" par M. Marc Delafontaine:

from the Author.

"Matériaux pour servir à l'histoire des métaux de la Cérise et de la Gadolinite:" par M. Marc Delafontaine:

from the Author.

"Recherches sur les Combinaisons du Niobium (deuxième mémoire) : " par C. Marignac : from the Author.

"La Vie et l'Œuvre de Charles Frédéric Gerhardt : " par J. H. F. Papillon : from the Author.

"Considérations sur la Science et les Savants : " par F. Papillon : from the Author.

"Introduction à l'Etude de la Philosophie Chimique : " par F. Papillon : from the Author.

"De l'Identité d'Origine, de Composition et de Propriétés Médicales des Sources Minérales du Bassin de Vichy : " par N. Larbaud : from the Author.

"Systematische Zusammenstellung der Organischen Verbindungen : " von C. Weltzien : from the Author.

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ERRATA.

- | Page. | Line. | for | publications | read | lectures. |
|-------|-----------------|--------------------------------|--|------------|---|
| 54 | 3 | | | | |
| 56 | 11 from bottom, | " | C ₄ | " | C ₂ |
| 56 | 4 from bottom, | " | C ₂ O | " | C ₂ O ₂ |
| 56 | 2 from bottom, | " | $\left\{ \begin{array}{c} C_2 \\ S_2O_4 \end{array} \right\}$ | " | $\left\{ \begin{array}{c} C_2 \\ S_2O_2 \end{array} \right\}$ |
| 380 | | " | $\left\{ \begin{array}{c} COO \\ Ba \\ COO \end{array} \right\}$ | " | $\left\{ \begin{array}{c} COO \\ Ba'' \\ COO \end{array} \right\}$ |
| 384 | bottom line, | " | isopropyllic acid, | " | isopropyllic alcohol. |
| 389 | | " | desoxalic series, | " | desoxalic or glyoxyloid series. |
| 392 | | " | diopside $\left\{ \begin{array}{c} SiO \\ SiO \end{array} \right\} CaO''MgO''$ | read | diopside $\left\{ \begin{array}{c} SiO \\ SiO \end{array} \right\} CaO''MgO''$. |
| 393 | top line, | " | ditanic, read | dititanic. | |
| 393 | | " | dolomite $\left\{ \begin{array}{c} CO \\ CO \end{array} \right\} CaO''MgO''$, | read | dolomite $\left\{ \begin{array}{c} CO \\ CO \end{array} \right\} CaO''MgO''$. |
| 393 | for | mercuroso-diammonic dichloride | $\left\{ \begin{array}{c} NH_3ClHg \\ NH_3ClHg \end{array} \right\}$ | read | mercuroso-diammo-
nic dichloride $\left\{ \begin{array}{c} NH_3ClHg \\ NH_3ClHg \end{array} \right\}$ |
| 394 | for | porcelain clay of Passau | $\left\{ \begin{array}{c} SiH_2O_2 \\ SiH_2O_2 \end{array} \right\} (Al'''_2O_4HO_2)^{iv}$ | read | porecelain clay of
Passau $\left\{ \begin{array}{c} SiH_2O_2 \\ SiH_2O_2 \end{array} \right\} (Al'''_2O_4HO_2)^{iv}$. |
| 394 | for | Lanarkite | $\left\{ \begin{array}{c} CO \\ SO_2 \end{array} \right\} PbO''_2$, | read | Lanarkite $\left\{ \begin{array}{c} CO \\ SO_2 \end{array} \right\} PbO''_2$. |

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